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☐ 1. Document ID: US 6509496 B1

L2: Entry 1 of 15

File: USPT

Jan 21, 2003

DOCUMENT-IDENTIFIER: US 6509496 B1

TITLE: Process for making mineral, food or pharmaceutical grade salt products

Detailed Description Text (7):

Once the reactants are placed in chamber 30, door 90a is closed, and the steam jacket is set to the first set point temperature typically from about 150.degree. F. to about 190.degree. F., preferably from about 155.degree. F. to about 189.degree. F., more preferably from about 160.degree. F. to about 188.degree. F., even more preferably from about 165 to about 185.degree. F. and most preferably about 180.degree. F. Other exemplary first set point temperatures include 150.degree. F., 155.degree. F., 160.degree. F., 165.degree. F., 170.degree. F., 175.degree. F., 180.degree. F., 185.degree. F., and 190.degree. F. The first and second set point temperatures disclosed herein are those appropriate for operation of the claimed process when operated at ambient pressure (e.g., 1 atmosphere). However, if the process is operated at lower than atmospheric pressure, the cycle time will be reduced optionally together with the first and/or second set point temperatures as would be readily understood by one of ordinary skill. The converse is also true. The first set point temperature adjusts the heat from the steam jacket such that the temperature of the contents of chamber 30 reach the first set point temperature. With the first set point temperature being set, the reactants in chamber 30 are mixed either with the plows 50 alone rotating about shaft 40 via motor 20 or with the aid of chopper blades 60a attached to choppers 60 and a chopper motor (not shown). Though not preferred, chopper blades 60a may sometimes be used alone. Typically, the shaft of chopper 60 is equipped with one or more chopper blades 60a, preferably three. Each chopper blade is preferably flat and in the shape of an "X" or "+". However, any suitable shape and number of chopper blades may be used to mix the reactants in the chamber 30. Further, the choppers are preferably used to "de-lump" the material within chamber 30 sufficient to avoid a separate "de-lumping" and/or drying step at the end of the claimed process. Such use of choppers 60 during the claimed process permits the final mineral, food or pharmaceutical grade salt product so made to be formed in a "de-lumped" formulation, which is directly amenable to a further grinding operation if necessary to satisfy a desired particle size distribution. By this inventive process, an intervening "de-lumping" step is avoided. Please note that the term "de-lump" is a term of art well understood by one of ordinary skill in the relevant art. The term "de-lump" means to reduce moist, semi-moist or dry solids down to grain size. See, for example, the brochure for DYNAMIC AIR TUFFER Aerator/Lump Breaker Series 329, incorporated herein by reference in its entirety.

Detailed Description Paragraph Table (1):

TABLE I LITTLEFORD PARAMETERS Time, hr (best PRODUCT Batch guess/ INFORMATION Raw

Size Little- Item Product Code Material Amount (Kg) ford) 1 Ca 91018210 Water 8.75 gal 100 1.5 Citrate Calcium 60.0 kg 21% Carbonate Citric Acid 68.1 kg 2 Mg 93005200 Water 4 gal 100 1.0 HVP Alcalase .083 kg 20% Aspartic 1.666 kg Acid Rice Protein 40.0 kg Citric Acid 15.133 kg MgO 37.7 kg (powder) 3 Ca 91006200 Water 4.5 gal 100 1.5 Amino- Aspartic 2.17 kg min Acid Ca 55.26 kg Carbonate Rice Flour 37.0 kg Citric Acid 17.39 kg 4 Mg 93018160 Water 12 gal 100 (2.5) Citrate Citric Acid 68.1 kg 16% MgO 29.0 kg (powder) 5 Mg 93402200 Water 4-8 gal 100 (2) Aspar- Aspartic 50.0 kg tate Acid 20% MgO 35.6 kg (powder) 6 Mg 93006200 Water 5 gal 100 1.25 Amino- Aspartic 2.17 kg min Acid 20% Rice Flour 34.78 kg Citric Acid 17.39 kg MgO 35.7 kg (powder) 7 K As- 95042227 Water 5 gal 100 2 partate K Carbonate 48.4 kg 22.7% Aspartic 72.0 kg Acid MgO 10.4 kg (powder) 8 Mg 93054152 Water 19.62 gal 100 3 Malate Malic Acid 62.5 kg 15.2% MgO 29.434 kg (powder) 9 Ca 91054230 Water 8.0 gal 100 3 Malate Malic Acid 77.0 kg 23% Calcium 60.0 kg Carbonate 10 Zn 97518300 Water 16.666 gal 100 2.25 Citrate ZnO 42.941 kg 30% Citric Acid 65.441 kg 11 Mg 93039160 Water 5-20 gal 100 (4) Krebs AKG .442 kg 16% Fumaric 17.714 kg Acid Malic Acid 17.714 kg Succinic 1.771 kg Acid Citric Acid 31.886 kg MgO 32.329 kg (powder) 12 Mg As- 93042084 Water 4-10 100 (3) partate Aspartic 82.8 kg 8.4% Acid MgO 16.2 kg (powder) 13 Ca 91027090 Water 3-6 gal 100 (2) Gluco- Calcium 26.1 kg nate Carbonate 9% GDL 81.27 kg 14 Zn 97506200 Water 5-10 gal 100 (2.25) Amino- Aspartic 2.17 kg min Acid 20% ZnO 25.0 kg Rice Flour 58.0 kg Citric Acid 17.39 kg 15 Ca 91039220 Water 4-10 gal 100 (2.5) Krebs AKG .12 kg 22% Calcium 60.0 kg Carbonate Fumaric 11.2 kg Acid Malic Acid 10.0 kg Succinic 4.0 kg Acid Citric Acid 51.0 kg 16 Ca 91048180 Water 4-10 gal 100 (2.5) Lactate Ca Carb./low 48.0 kg 18% Pb Lactic Acid 94.0 kg 17 Mg 93027050 Water 4-10 gal 100 (2.5) Gluco- GDL 96.9 kg nate 5% Mg Carbo- 23.37 kg nate 18 Mn 93518280 Water 4-15 gal 100 (3.5) Citrate Mn Carbo- 67.44 kg 28% nate Citric Acid 50.0 kg 19 Se 95506010 Water 5-15 gal 100 (3.5) Amino- Aspartic 5.0 kg min 1% Acid Sodium 2.8 kg Selenite Rice Flour 75.0 kg Citric Acid 10.0 kg MgO 10.0 kg (powder) 20 Ca 91058114 Water 4-15 gal 100 (3.5) Orotate Ca Carbo- 29.23 kg 11.4% nate Orotic Acid 88.6 kg 21 Ca Mg 10227 Water 8 gal 100 1.25 Amino- Aspartic 3.044 kg min Acid 24/12 Ca Carbo- 37.594 kg nate Lime 20.443 kg (CaOH.sub.2) Rice Protein 1.044 kg Rice Flour 5.158 kg Citric Acid 4.278 kg MgO 23.689 kg (powder) 22 Cu 92027130 Water 4-8 gal 100 (2.5) Gluco- Cu Carbo- 30.0 kg nate nate 13% GDL 90.0 kg 23 K Suc- 95075330 Water 2-8 gal 100 (2) cinate K Carbo- 58.62 kg 33% nate Succinic 50.09 kg Acid 24 V Krebs 97039005 Water 3-11 gal 100 (3) 0.5% AKG .03 kg Fumaric .49 kg Acid Malic Acid .49 kg Succinic .03 kg Acid Vanadium 1.05 kg Pentoxide Citric Acid .99 kg DCP- 97.99 kg Calcium (Anhydride) 25 Mo 94039005 Water 5 gal 100 (1.5) Krebs AKG .03 kg 0.5% Fumaric .49 kg Acid Malic Acid .49 kg Sodium 1.538 kg Molydate Succinic .03 kg Acid Citric Acid .99 kg DCP- 98 kg Calcium (Anhydride) 26 Ca 102200 Water 3-9 gal 100 (3) Asporo- Aspartic 56.908 kg tate Acid 20% Ca Carbo- 40.908 kg nate Lime 18.0 kg (CaOH.sub.2) Whey Con- 2.726 kg centrate Citric Acid 4.545 kg 27 Mg 102250 Water 4-15 gal 100 (3.5) Asporo- Aspartic 42.68 kg tate Acid 20% Whey Con- 2.328 kg centrate Citric Acid 3.88 kg MgO 41.128 kg (powder) 28 Mg 93075170 Water 4-15 gal 100 (3.5) Succin- Succinic 44.9 kg nate Acid 17% Citric Acid 14.012 kg MgO 30.9 kg (powder) 29 Mn 93542170 Water 4-15 gal 100 (3.5) L-ASP Aspartic 82.0 kg 17% Acid Mn Carbo- 41.86 kg nate AKG = Alphaketoglutaric GDL = Glucono Delta Lactone Ca Carb./low Pb = Calcium Carbonate/Low Lead DCP Calcium = Dicalcium Phosphate Calcium

Full	Title	Citation	Front	Review	Classification	Date	Reference	Abstract	Claims	KMIC	Draw De
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2. Document ID: US 3796663 A

L2: Entry 2 of 15

File: USOC

Mar 12, 1974

DOCUMENT-IDENTIFIER: US 3796663 A
TITLE: LUBRICATING OIL ADDITIVES

h e b b g e e e f e c c e c ec

one of these properties is required in the same product. DESCRIPTION OF THE PREFERRED EMBODIMENTS The N-hydroxy hydrocarbyl-substituted cyclic imides of C₄---CB dicarboxylic acids are of the general formula $\text{O} \text{---} \text{R} \text{---} \text{CH} \text{---} \text{N} \text{---} \text{O} \text{---} \text{C}(\text{CH}_2)_b \text{---} \text{C}$ wherein a and b are integers, a is equal to 0, 1 or 2, b is equal to 0, 1 or 2, a+b is equal to 1 or 2, and R is an aliphatic or alicyclic hydrocarbyl of from 10 to 30 carbon atoms. (By hydrocarbyl is intended a monovalent organic radical composed solely of carbon and hydrogen, which may be aliphatic, alicyclic or aromatic, or combinations thereof.) Usually, the hydrocarbyl will be alkyl or alkenyl, the hydrocarbyl being derived from petroleum and its nature dependent to a large extent on the reaction by which the hydrocarbyl-substituted succinic acid is prepared. This reaction usually involves the addition of an olefin to maleic acid or anhydride, in which case the double bond of the maleic acid anhydride becomes saturated and there remains in the hydrocarbyl at least one olefinic double bond. If it is desired, the olefinic bonds may be saturated by hydrogenation. Preferably an alpha-olefin, such as those obtained from cracking wax (cracked wax olefins), is reacted with maleic anhydride to form an alkenylsuccinic anhydride. This product may then be hydrogenated to form the alkylsuccinic anhydride. The methods of reacting an olefin with maleic anhydride are well known in the art and do not require exemplification here. Illustrative of various alphaolefins which may find use are 1-decene, 1-undecene, 1dodecene, 1- tridecene, 1-tetradecene, 1-pentadecene, 1hexadecene, 1-heptadecene, 1- octadecene, 1-nonadecene, 1-eicosene, 1-heneicosene, etc. When the addition reaction with maleic anhydride is utilized, or otherwise, it is often preferable to use as the olefinic hydrocarbon reactant a low molecular weight polymer or copolymer of C₂-C₄ olefins, i.e., an oligomer of C₂-C₄ olefins. Such oligomers are, for example, tetrapropylene, triisobutylene, tetraisobutylene, etc.; these polymers are mono-olefins of a straight- or branched chain structure,

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31796,663 3 Method of preparation A preferred method of preparing the reaction product of this invention is the addition of the oligomer tetrapropylene or hexapropylene to maleic anhydride followed by reaction of the addition product with hydroxylamine 5 generated in situ from hydroxylamine hydrochloride and triethylamine; other bases, such as calcium hydroxide, pyridine, or MgO may also be useful. $\text{O} \text{---} \text{R} \text{---} \text{CH} \text{---} \text{C} \text{---} \text{O} + \text{TTONTT3Cl} + \text{Et}_3\text{N} \text{---} \text{Z} \text{---} \text{O} \text{---} \text{R} \text{---} \text{CH} \text{---} \text{C} \text{---} \text{O} \text{---} \text{H} + \text{Et}_3\text{NHCl} + \text{H}_2\text{O}$ Because of the high viscosity of this system and the exothermicity of the reaction, a solvent such as toluene or a petroleum-based ant thinner is desirable. In a typical reaction, one heated equimolar portions of the anhydride and hydroxylamine hydrochloride with about 10 percent excess triethylamine in toluene, amounting to about 20-80 percent of the total mixture. When the temperature reached about 90-100° C., a strong exotherm occurred, rapidly raising the temperature to about 120- 30 30° C. The reaction was largely completed when the exotherm decreased, but was usually continued for an additional 1-3 hours at 100-140° C. The by-product, triethylammonium chloride, was washed out with water, but filtration is also a possible method of separation. Azeotropic distillation with toluene can be used to remove the water of reaction. The hydroximide was identified by nitrogen analysis, titration with base (the hydroximides titrate as weak acids), and by infrared spectra, which showed the 40 loss of anhydride absorption and a gain of cyclic imide absorption. The following examples illustrate the reaction conditions, reactants and products of the present invention, but are offered for purposes of illustration rather than limitation. Example 1 50 g. (approximately 0.1 mole) of cracked wax alkenylsuccinic anhydride, of C₁₅-C₂₀ cracked wax olefin (equivalent weight 250), was reacted with 7.1 g. (approximately 0.1 mole) of hydroxylamine hydrochloride and 11 g. (approximately 0.11 mole) of triethylamine in 100 g. of toluene. The reaction proceeded at 110-115° C. for approximately 2 hours. The yield of product was 38 g. of waxy material, 2.3 percent nitrogen (2.7 percent calculated). IR analysis of the product showed the presence of imide bands at 1780 cm.⁻¹ and 1720 cm.⁻¹. Example 2 140 g. (approximately 0.4 mole) of cracked wax 60 alkenylsuccinic anhydride, of C₁₅-C₂₀ cracked wax olefin (equivalent weight 175), was mixed with 29

g. (approximately 0.4 mole) of hydroxylamine hydrochloride and 43 g. (approximately 0.42 mole) of triethylamine in 60 g. of toluene. The reaction mixture was reacted at 90-120° C. for about 2 hours. The yield of product was 43 g. of waxy material, of 2.3 percent nitrogen (3.8 percent calculated). IR analysis of the product showed the presence of imide bands at 1780 and 1720 cm.⁻¹. Example 3 264 g. (approximately 1 mole) of tetrapropenylsuccinic anhydride was mixed with 71 g. (approximately 1 mole) of hydroxylamine hydrochloride and 11 g. (approximately 1.1 moles) of triethylamine in 150 g. of toluene. The mixture was reacted at 110-130° C. for about 3 hours. The yield of product was 228 g. of resinous material, of 4.28 percent nitrogen (4.99 calculated). IR analysis of the product showed the presence of imide bands at 1780 and 1710 cm.⁻¹. Example 4 37 g. (approximately 0.1 mole) of hexapropenylsuccinic anhydride was mixed with 7.1 g. (approximately 0.1 mole) of hydroxylamine hydrochloride and 11 g. (approximately 0.1 mole) of triethylamine in 50 g. of toluene. The mixture was reacted at 90-115° C. for about 2 hours. The yield of product was 35 g. of viscous liquid, of 3.26 percent nitrogen (3.7 percent calculated). IR analysis of the product showed the presence of imide bands at 1780 and 1715 cm.⁻¹.

Rust Inhibition Results from three types of rust tests are given in Tables I and II.

TABLE I [Turbine Oil-Seawater Rust Test (ASTM D 665) and Demulsibility Test (ASTM D 1401)]

Concentration	Percent Emulsion	Additive	Rust	Vol. 2	None	(base oils)
100	0	Cracked wax alkenylsuccinic hydroxide	4			
0.1	0	Do. 5		0.04	0	63

Tetrapropenylsuccinic hydroidimide --- 0.1 0 0 Hexapropenylsuccinic hydroxide --- 0.1 25 --- Percent by weight in base oil. Volume in milliliters. 3 Turbine oil base heavy, 470 SSU at 100° P. and 61 SBU at 210° F. 4 Cracked wax olefin of Example 1. 5 Cracked wax olefin of Example 2.

TABLE II [Humidity Cabinet Rust Test (ASTM D 1748) and Outdoor Exposure Test]

Concentration	Humidity	Outdoor	Additive	Exposure	Time	in time
16	<1	Myristic acid		8	None	(base oil 4)
>3		Cracked wax alkenylsuccinic hydroxide	5			
1	110	Tetrapropenylsuccinic hydroxide				
1	150	I-rexapropenylsuccinic hydroxide				<1

Percent by weight in base oil. @, Protection time, in hours, of sandblasted steel panel. 3 Protection time, in weeks, of sandblasted steel panel. 130 SSU, 1001 F., neutral oil. C15-C20 cracked wax olefin. Hydroxide solubilized in base oil with 7 percent 2-ethylhexanol. Both tetrapropenyl and cracked wax alkenylsuccinic hydroxides passed the Turbine Oil-Seawater Rust Test (ASTM D 665) and the Demulsibility Test (ASTM D 1401). Rust inhibition and compatibility with other additives were excellent. In the Humidity Cabinet Rust Test (ASTM D-1748), both branched and linear carbon chain hydroxides gave better rust inhibition than carboxylic acids such as myristic acid or tetrapropenylsuccinic acid. The outdoor exposure test was conducted on sandblasted steel panels exposed to the Northern California rainy season. A linear carbon chain hydroxide inhibited rust better than a calcium sulfonate widely used as a lubricant additive. Effects on friction and wear Additives that reduce static friction are valuable in industrial lubricants because they also reduce the power requirements for starting machinery. A typical additive that performs this function is myristic acid. We compared

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5 hydroxides with myristic acid in the Godfrey Tribometer (ASLE Transactions, 7, 24-31 (1964)). In this device a SAE 52100 steel needle from a needle bearing was pressed vertically against the side of a rotating ASI 4615 steel Timken roller bearing cup; a strain gauge measured the friction between them. Results in Table III show that both myristic acid and a cracked wax alkenylsuccinic hydroxide reduced static friction by 47 percent. TABLE III [Friction and wear tests]

Coefficient of friction	Needle wear	% A static	% A volume	Additive	I Kinetic	Static
0.16	0.19			1.6		
0.10	0.10	-47	1.4	Trieresyl phos- pbate		9.12 0.
-32	0.47	-70		cracked wax alkenylsuccinic hydroxide	I---	0.11 0.10 -47 0.50 -69
				Tetrapropenyl- succinichydroxide		0.13 0.16 -16 0.99 -38

Hexapropenyl- succinic hydroxi- niide ----- 0.13 0.22 +17 0.50 -69 I
 Additives at 1% by weight in base oil. 20odfroy Tribometer; A static measured
 relative to base oil; load of kg.; speed of 0.4 fpm; time, 2 hours. 3 Godfrey
 Tribometer; A volume measured relative to base oil; volume In units of 10-1 nun.'. 4
 Base oil; 130 SSU, 100 F., neutral oil. 5ClIC20 cracked w" olefin. Hydroxinitde
 solubilized in base oil with 7% of 2- othylhexanol. Antiwear agents are valuable in
 lubricants for applications in which full hydrodynamic lubrication does not always
 exists A typical steel/steel antiwear agent is tricresyl phosphate. It reduced
 needle tip wear in the Godfrey Tribometer test by 70 percent. The cracked wax and
 per- hexapropenylsuccinic hydroximides reduced it by 69 cent and the
 tetrapropenylsuccinic hydroximides reduced wear by 38 percent. Thus, the
 hydroximide can reduce both friction and wear as well as each specialized additive,
 besides inhibiting rust. The specialized additives mixed together in a lubricant
 for these separate functions would compete with each other for the metal surface,
 consequently some properties would suffer. Another frictional property of interest
 is the relative static and kinetic coefficients of friction between the fibrous and
 steel members of clutch plates in an automatic transmission. General Motors
 requires automatic transmission fluids (ATF) that produce lower static than kinetic
 friction. Ford requires the opposite relationship, i.e., higher static than kinetic
 coefficients of friction. It has been found that cracked wax alkenylsuccinic
 hydroximide meets the General Motors requirement and the tetrapropenylsuccinic
 hydroxide meets the -Ford requirement in simple oil solutions. That is, the
 coefficient of friction decreases with increasing speed for the tetrapropmyl-
 derivative solution aind shows the opposite behavior for the cracked wax alkenyl
 derivative solution. The multifunctional action of the N-hydroxy hydro. carbyl-
 substituted cyclic imides :of C4-C5 dicarboxylic acid (e.g., hydrocarbyl-
 substituted @uceinic hydroximides) offers a potential solution to the problem of
 combining several film-forming properties in one lubricant while avoiding
 competition among separate additives for the same surface. These hydroximides are
 useful lubricating 31796,663 6 transmission fluids and preservative oils requiring
 antirust, antiwear, and friction- modifying properties. The coniposit ions of this
 invention may be used with a wide variety of lubricati ng media, including oils of
 lubricating. viscosity, as well as greases. Various base oils which find. use
 include oils such as petroleum lubricating oil; naphthenic base, paraffin base, and
 mixed based; syn- thetic oils; alkylene polymers and alkylene oxide polymers-
 ,esters of organic and inorganic acids; acryl hy- 10 drocarbons ,and ethers;
 organic silicone compounds ; etc. The base oils can be used individually or in
 combinatio n, wherever miscible or wherever made so by the use of mutual solvents.
 The additives of the present invention will be present 1.5 in lubricating oils and
 greases in concentrati ons of from 0.01 to about 5 percent by weight, and
 preferably 0.05 to about 3 percent by weight. In addition, these lubricating
 compositio ns may also contain other lubricating oil and grease additives such as
 oiliness agents, extreme- pressure agents, rust inhibitors, oxidation inhibitors,
 corrosion in- 20 hibitors, Viscosity index improving a-gents, dyes, detergents,
 dis@ersant s, etc. The total amount of these additives will usually range from
 about 0.1 to 20 percent by weight, and more usually from about 0.5 to 10 percent by
 weight. 25 The individual additives may vary in amounts from about 0.01 to 10
 weight percent of the total compositio n. A s wi 'II be evident to those skilled in
 the art, various modifica tions of this invention can be made or followed in the
 light of the foregoi ng discussio n and disclosur e 30 without departing from the
 spirit or scope of the disclosure or from the scope of the following claims. claim:
 1. A lubricati ng oil composit ion containin g from 0.5 to 20 weight percent of a
 N- hydroxy alkyl or alkenyl 35 cyc" c imide of a C4 dicarboxyli c acid. 2. A
 lubricati ng oil composit ion containin g from 0.5 to 20% by weight of a composit
 ion of the general formula $O_4O(CHI)_a - C(R) - O @ N O H (C H_2)_b - C O$ wherein a
 and b are integers, a is equal to 0, or 1, b 45 is equal to, or 1, a plus b is
 equal to 1, and R is alkyl or alkenyl group of from 10 to 30 carbon atoms. 3. A
 lubricati ng oil composit ion accordin g to claim 2 wherein R is selected from the
 group consisting of tetrapropenyl and hexapropenyl . 50 4. A lubricating oil
 compositio n according to claim 2 wherein @R is derived from olefin of average

molecular weight in the range from 100 to 500, R e f e r e n c e s C i t e d 55
 UNITED STATES PATENTS 2,279,560 4/1942 Dietrich ----- 252-51.5 A 2,279,973
 4/1942 Dietrich ----- 252-51.5 A 3,407,204 10/1968 Shay et al - ----- 252-51.5
 A 60 3,367,959 2/1968 Fetscher et al. ---- 252-51.5 A WERTEN F. W. BELLAMY, Primary
 Examiner U . S . C l . X . R . oil additives in industrial and automotive
 lubricants, 65 260-326.5J , 326.5 F, 326.5 FM

Full	Title	Citation	Front	Review	Classification	Date	Reference	Abstract	Claims	MMIC	Draw De
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3. Document ID: US 3708398 A

L2: Entry 3 of 15

File: USOC

Jan 2, 1973

DOCUMENT-IDENTIFIER: US 3708398 A

TITLE: FERMENTATION PROCESS FOR THE PRODUCTION OF CITRIC ACID

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3 In those cases where substantial amounts of citric acid are produced, the acid is generally isolated as the insoluble calcium citrate by methods well known to those in the art. The outstanding advantage of the instant fermentation process over those previously used for the production of citric acid is its simplicity and rapidity. The yeast inoculum may be prepared by propagating the yeast cells from a slant for about 24 hours under aerobic conditions in an aqueous fermentation medium containing an assimilable carbohydrate, generally glucose; an assimilable nitrogen source, preferably peptone; yeast extract; and sodium chloride. The broth is usually a.-itated at room temperature during the fermentation, and the final pH of the medium at the end of the 24 hour period is usually about 4.5. The rate of growth of the yeast cells is periodically determined by centrifuging the broth for 15 minutes at about 2000 g. Generally, a yeast cell density (spindown) of 0.5 ml. of yeast cells per 15 ml. of broth is preferred before the broth is used for inoculation. After agitating the above inoculation culture at room temperature for about 24 hours, a portion of it is added to the aqueous fermentation medium, which contains a carbohydrate and source of assimilable nitrogen. We prefer such carbohydrates as potato or corn starch, molasses, sucrose, glucose, maltose, dextrin, fructose, and galactose. Because of its availability and low cost we generally prefer to use a molasses as the carbohydrate source, and we use amounts equivalent to as much as 28% by weight of sugar. A further highly significant advantage of the process of the present invention lies in the fact that pretreatment of the molasses for metal ion control is unnecessary. As is well known, prior art citrate fermentations which utilize molasses or ordinarily sensitive to the metal ion contaminants and require that the molasses be pretreated and appropriately purified before use. See for example, D. S. Clark, Industrial and Engineering Chemistry Product Research and Development, 1, 59 (1962). As an available nitrogen source, such nitro-en-containing organic materials as wheat bran, soybean meal, urea, amino acids, peptones, and enzymatically digested proteins, can be used. We have found the commercially available product =, a casein peptone source available from the Sheffield Chemical Co., Norwich, N.Y., to be a convenient source of assimilable nitrogen. We generally use from 1 to 20 g. of this peptone source per liter of medium. Inorganic compounds may also serve as sources of assimilable nitrogen. Of these we prefer ammonium nitrate, ammonium sulfate and ammonium chloride. The following mineral cations and anions are also considered beneficial for the growth of the yeasts: sodium, potassium, cobalt, phosphate, and sulfate. It is well known that trace amounts of various vitamins such as biotin also play a role in cell growth. Most of these trace vitamins and essential minerals are present as impurities in the crude nitrogen and carbon sources, and

consequently it is not usually necessary to add them individually to the fermentation medium. Calcium carbonate also promotes the growth of the yeast cells and is generally added to the medium. The fermentation is allowed to proceed aerobically, usually for about 72 to 120 hours with agitation, at a temperature from about 20 to 37° C., although a temperature of about 25° C. is preferred. While any form of aerobic incubation is satisfactory, controlled aeration, as for example agitation under air, or passing air through the fermentation medium, is generally employed. Although we prefer to carry out the fermentation aerobically, it is also possible to perform it under anaerobic conditions using an oxidizer other than oxygen as the terminal hydro-, -en acceptor. During the course of the fermentation the pH of the medium is maintained anywhere from about 1.5 to 3.0, although a pH range of about 2.0 to 7.0 is preferred. We have found that during the initial stages of the fermentation the pH should preferably not be too low, e.g., not less than about 3.0, otherwise there will be insufficient yeast growth. When, however, sufficient yeast growth has been established, the pH is then maintained within the limits given above. When substantial amounts of citric acid are produced, the acid may be isolated from the fermentation medium by various methods well known to those skilled in the art. As mentioned above, we generally prefer to incorporate calcium carbonate in the fermentation medium, usually an amount of from 5 to 25 g. per liter of fermentation medium. As the citric acid forms, it reacts metathetically with the calcium carbonate, yielding carbon dioxide and insoluble calcium citrate, which can then be conveniently removed from the fermentation medium. It appears that some of the liberated carbon dioxide is metabolized by the yeast cells and thus promotes their growth in the medium. Instead of CaCO₃, one can also use BaCO₃, BaO, CaO, NaOH, and KOH. It should be understood that when reference is made herein and in the claims to recovering citric acid from the medium, this expression is intended to embrace recovery in the form of a salt, such as the calcium salt, as well as recovery as citric acid per se. The salts can be conveniently converted to the free acid by methods well known to those skilled in the art. In the present invention, a citric acid-accumulating yeast is defined as one which will accumulate at least one gram of citric acid per liter of medium under the fermentation conditions described. The use of a yeast strain that accumulates less than one gram of citric acid per liter of medium is of little or no practical value. Analytical techniques and methods of analysis for the determination of citric acid are described as follows: METHODS OF ANALYSIS (1) Paper chromatography The systems below provide a convenient semi-quantitative means for determining citric acid in the fermentation medium. Concentrations of citric acid even lower than 1 gram per liter of medium, i.e., 1 mg. per ml. of medium, can be readily detected by these chromatographic methods. (1) Solvent system A This solvent system is a mixture by volume of 80 parts methyl ethyl ketone, 6 parts acetone, 12 parts distilled water and 2 parts formic acid. Citric acid exhibits an R_f of about 0.59 to 0.64 with this system. (2) Solvent system B This solvent system consists of by volume 1 part 55 formic acid, 2 parts cineole, and 3 parts n-propanol. The R_f of citric acid with this system is about 0.40 to 0.45. (3) Solvent system C This solvent system consists of a water-saturated 60 formic acid-ether mixture prepared by shaking together in a separatory funnel a mixture consisting of 2100 ml. of ethyl ether, 300 ml. of formic acid, and 275 ml. of water. After shaking, the upper solvent layer is used as the chromatographic solvent. The R_f of citric acid, with this system is about 0.30 to 0.35. A 5 to 10 microliter sample of the fermentation medium, which has been treated as described above is placed on the paper, and the chromatogram run in the usual manner. We generally use Whatman No. 1 paper as the adsorbent and Bromocresol Green as the indicator (prepared by dissolving 0.25 g. of Bromocresol Green in 400 ml. of acetone and adjusting the solution to green color) in these analyses. In all cases an authentic sample of citric acid is run with each chromatogram as a standard.

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3708)398 5 (11) Acetic anhydride-pyridine analysis This method is described by J. R. Marier and M. Boulet in J. Dairy Sci., 41, 1683 (1958). Because of its

simplicity, we generally prefer to use this method to determine -quantitatively the amount of citric acid 5 in the medium. After treating the 25 ml. fermentation medium used in the screening as described above, the filtrate or super- natant is diluted with 0.1 N HCl to 100 ml. Aliquots of this stock solution are than analyzed for citric acid in 10 the manner described in the above article. (IH) Gas chromatography Another quantitative method for determining citric acid 15 that we have used is a modification of a method - described by N. W. Alcock, Anal. Biochem., 33, 2 (1965). This analysis is carried out with an F and M model 500 gas chromatograph fitted with F and M model 1609 flame ionization detector under the following conditions. 20 Column-Alu,minum, 6' x 1/4" packed with 5% DEGA on ABS Column T-170' C. Injection port T-260' C. Detection block T-260' C. 25 Helium flowrate-10.5 reading on Brooks - R-2-15AAA flowmeter Hydrogen flowrate-8.0 reading on Brooks - R-2-15AAA flowmeter Air flowrate-12.0 reading on Brooks R-2-15AAA flow- 30 meter Sample size-5 microliters A standard curve is prepared by first weighi ng out exactly the following amounts of citric acid: 50, 100, 150, 35 200 and 300 mg. To each of these samples is added 10 ml. of boron trifluoride dissolved in a small amount of ethanol. The mixture is heated at 90' for 10 minutes and cooled. Each sample is added to a separatory funnel con- taining a mixture of 10 ml. of distilled water and 4 ml. 40 of chloroform and vigorously shaken for 30-40 seconds. The lower chloroform layer is separated and added to a Teflon-lined, screw-capped 10 ml. test tube. The aqueous phase in the separatory funnel is extracted with two 3-ml. portions of chloroform which are also added to the test 45 tube. A 5 microliter portion of each sample is injected into the chromatograph and a standard curve is prepared by plotting the amount of citric acid as abscissa and the corresponding peak areas of the chromatogram as ordi- nate. The determination of the peak areas are conven- 50 iently calculated by means of an integrator attached to the Gas Chromatograph. A sample eof the fermentation medium is then taken, the pH adjusted to about 2.0 with concentrated hydro- chloric acid, and the mixture either centrifiged or filtered 55 to remove suspended matter. To 5 ml. of the clear solu- tion is added 20 ml. of 2,2-dimethoxypropane. The result- ant solution is then evaporated to dryness on an open water bath, set at 60-80' C. To the dry residue is added 10 ml. of boron trifluoride in methanol. This solution 60 is treated exactly in the same manner as the standard above. The amount of citric acid in the sample is readily caiculated by comparison with the standard curve. It is to be further understood that the process of the present invention also embraces the use of yeast mutants 6,5 or varians produced by various chemical and physical means, provided, of course, that they exhibit the specified citric acid- accumulating ability. Such mutants are produced by techniques such as X- ray and UV radiation; treatment with nitrogen mustards and organic peroxides; 70 and other similar techniques well known to those skilled iD the art. In addition, the use of subcultures, natural mutants, variants and the like, is contemplated in carrying out the pi-ocess of the present invention. 75 6 The following examples are provided to more fully illustrate the present invention, but are not to be construed as limiting the scope thereof. Preparation of inoculum A slant containing yeast cells is transferred to 50 ml. of liquid Sabouraud's medium contained in a 300 ml. Erlenmeyer flask. The flask is incubated on a rotary shaker for 2-3 days at 28' C. EXAMPLE I Fifty ml. of inoculum of the citric acid-accumulating yeast strain, Rhodotorula rubra CMI 38784 prepared as described above, is added to an aqueous, sterilized nutrient medium containing the following ingredients: Grams/liter Crude sugar from cane molasses ----- 135.0 Cotton seed meal ----- ----- 3.0 Calcium carbonate ----- 13.0 Urea ----- ----- 8.0 Urethane polyether resin (Voranol, Dow Chemi- cal) ----- ml-- 0.2 Lead acetate ----- 0.1 No pH adjustment. Autoclaved 30 minutes at 121' C. Fluoracetamide I ----- ----- 0.1 Lead acetate 2..... 0.5 I Added after antoclaving. Added at 9 hours. The inoculated m@idium (2 liters contained in a 4 liter stirred fermenter) is incubated at 28o C. with aeration at a rate of 0.75 volumes of air per volume of medium per minute and stirring at 1750 r.p.m. After 5 days the fermentation yield of citric acid is 18.4 grams/liter, and the citric acid is recovered. EZXAMP-LE][I The process of Example I is repeated in turn with each

of the following yeast strains: Sporobolomyces sp. ATCC No. 2029 1, Nematospora coryli ATCC No. 20292, Rhodotorula glutinis ATCC No. 2527, Sporobolomyces sp. ATCC 20290, Zygosaccharomyces mellis NRRL Y-1053, Sporobolomyces salmonicolor CBS 490, Torula racemosa ATCC No. 20288 and Torula racemosa ATCC No. 20289. The fermentation medium of Example I is modified as follows: Grams/liter Crude sugar from cane molasses ----- 270.0 Cotton seed meal ----- 3.0 Calcium carbonate ----- 13.0 Urea ----- 10.0 No pH adjustment. Autoclaved 30 minutes at 121' C. Fluoracetamide I ----- 0.1 Le,ad acetate 2..... 0.2 I Added after autoclaving. Added at 9 hours. Results obtained with each of the indicated yeast strains are shown in the following table: Fermen- Citric Public culture tation acid depository tiine (gms./ Yeast strain No. (days) liter)

Yeast strain	ATCC No.	gms./ liter	days
Sporobolomyces sp	ATCC No. 5 71.3 20291. A ematospora COTYli	5	71.3
ATCC No. 5 73.8 20292. Rhodotorula glutinis	ATCC No. 2527-	5	73.8
91.0 Sporobolomyces Sp	ATCC No. 5 89.3 20290. Zygosaccharomgfc	5	89.3
mellir	NRRL Y-1053--	5	18.3
43.0 TOTula ramosa	ATCO No. 3 30.0 20288 Do	3	30.0
----- ATCO No. 3 33.0 20289			

Full	Title	Citation	Front	Review	Classification	Date	Reference	Claims	KNWC	Draw De
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4. Document ID: US 3663720 A

L2: Entry 4 of 15

File: USOC

May 16, 1972

DOCUMENT-IDENTIFIER: US 3663720 A

TITLE: ARTICLE OF MANUFACTURE HAVING HIGH TEMPERATURE RESISTANT PROPERTIES AND METHOD OF MAKING THE SAME

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3)663,720 3 The water of condensation serves to set the hydraulic cement also included in the composition. The term "hydraulic cement" is used in the specification to include those inorganic cements which harden by the addition of water. The preferred hydraulic cements are .5 the various kinds called portland cement. I have @found that silicate containing cements are superior to those which do not contain silica in combined form. According- ly, even silica flour may be used in the present invention as well as other sources of silica gel. Aluminous - cements 10 may also be used, as well as natural cements. Gypsum cements, such as plaster of Paris, Keene's cement, etc. are less suitable for use in the invention as the hydraulic cement because of the lack of silica or silicate ion. As is well known, portland cements are composed chief- 1,5 ly of three oxides: silica (SiO₂), lime (CaO), and alumina (Al₂O₃), with small quantities of MgO, SO₃, and Fe₂O₃ also present. ifour principal compounds are recognized in portland cement. They are: tricalcium silicate 20 (3CaO-SiO₂) dicalcium silicate (2CaO-SiO₂); tricalcium aluminate (3CaO-Al₂O₃); and tetracalcium aluminoferrite (4CaO-Al₂O₃-Fe₂O₃) 25 These four compounds are combined into various pro- portions to form the five generally recognized types of portland cement. These five types are defined by the American Society for Testing Materials in ASTM C 150- 30 61. While allfive types of portland cement may be used to advantage in the instant process, type 11 is preferred. In fact, various combinations other than the five defined types of cement may be used. That is, additives and vari- ations in the proportions may be accommodated to meet 35 the particular and specification intended. Changes niay be incorporated into the cement formulation to control the rate of settin-, the ultimate strength, the heat of hy- dration, the volume stability and the durability of the cement. The art of manufacturing portland cement is well 40 developed and documented in the

literature, for example, "The Portland Cement and Asphalt Concretes" by Thomas D. Larsen, McGraw-Hill, 1963. Depending upon the reactivity of the hydraulic cement, between about 2 and 6% hydraulic cement, based on the weight of the resin, should be added. Greater amounts of cement accelerate the hardening of the composition and thereby shorten the pot life. While citric acid or other retardant to polymerization may be added, it is preferable to maintain the amount of cement below 6%. - Greater amounts, when used, simply produce a quick setting of the cement without any increase in strength. By employing the cement within the preferred range, the resulting composition is substantially stronger than the cement alone. The strength of the polyhydric phenol-formaldehyde resin when combined with 2 to 6% cement has an average flexural strength of 15 to 20,000 pounds per square inch. The flexural strength goes as high as 27,000 pounds per square inch or higher, with the tensile strength being as high as 30,000 pounds per square inch. In contrast, Portland cement alone generally has a strength less than 10% of my new composition. Moreover, the combination of cement and resin produces a composition stronger than either of the ingredients alone. That is, my improved composition provides flexural strength and tensile strength 65 greater than that of resorcinol-formaldehyde systems generally. The amount of cement that may be added to the polyhydric phenolic resin system varies with the reactivity of the cement. At least 2% cement is required in order to obtain the desirable properties of the resultant composition. I have found that a presence of the cement serves as a viscosity depressant in the resin system. This result is surprising because the powdery nature of the added cement would be expected to increase viscosity. 75 4 It is not precisely understood why the viscosity of the resin-cement is lowered. Such a reduction in viscosity occurs only within rather narrow limits, depending upon the precise resin used, the hydraulic cement used and the various additives employed. If a large quantity of portland cement, say 20% is added to resorcinol-formaldehyde resin, the whole mass heats up and solidifies into an unmoldable mass. Greater than 4% portland cement thickens resorcinol-formaldehyde resin and less than 3% produces a lesser effect on the viscosity. Under 2% hydraulic cement provides no benefit and is negligible in effect on the ability of the resin to saturate fibers. On the other hand, the presence of more than about 10% cement reduces the strength of the mixture substantially. In addition, the composition sets up so rapidly that it is difficult to handle and use. One of the principal advantages of the present invention is the ease of handling of the aqueous non-burnable system. Between 2 and 6% cement, based on the weight of the resin, is generally necessary to obtain the improved properties described above. The preferred amount of cement in the composition is between about 3 and 4%, based on the weight of the resin. This amount furnishes an easily handled, nonburnable composition which is adaptable to a large number of uses. Where the cement used is fresh and particularly reactive, 3 % is generally the optimum amount. However, with less reactive types of cement and with cement which is not as fresh, 4% cement is generally the optimum amount. A number of additives may be included in the resin composition depending on the uses contemplated. Thus, where the composition is used as a molding resin, the existence of fibrous materials is particularly desirable. Cottonseed hulls, nylon fibers, wood fibers, glass fibers, etc. are well adapted to be used with the resin-cement combination. Not only do these fibrous materials extend the resins, they serve to decrease the brittleness of the hardened resin. A traditional problem with resorcinol-formaldehyde resin systems has been their inability to wet fibrous materials. However, the presence of cement in the composition of the present invention serves to lower viscosity and increase the wetting power of the resin system so that it will saturate the fiber and produce a strong bond with the fibers. The presence of fibrous material, while not mandatory, serves to control the shrinkage of the resin and to prevent cracking or crazing of the resin when molded. Other additives such as calcium carbonate, talc, wood flour, and similar fillers may be added if desired. However, many fillers are burnable, so that the non-burning characteristics of the composition of the present invention are reduced by the addition of burnable fillers. Commercially available formaldehyde and paraformaldehyde often contains wood flour. It is preferable to use

paraformaldehyde without wood flour, but small amounts of the filler are acceptable where the anticombustion properties of the resin-cement combination are not as critical. A graphite powder may conveniently be added to the resin composition of this invention to impart a flexible property to the cured product. In some applications, the added flexibility is desirable. In addition, the graphite powder serves as an extender without adversely affecting other properties of the composition. The high heat resistance of graphite is also an important property for use in some applications. Generally speaking, between 20 and 40 percent to added graphite powder is necessary to add flexibility to the cured product. However, lesser amounts may be used to extend the resin. Greater than 40 percent may also be added, although the increase in flexibility is negligible. The resin composition of the present invention may be utilized in many basic manufacturing processes. For ex-

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3,663,720 5 ample, conventional extrusion equipment may be used to provide soil pipe which is competitive in price to drain tile and Orangeburg. Extrusion equipment can also produce underground conduits for either electrical purposes or otherwise. Also, ducts for either hot air or cold air may be extruded using conventional equipment with the present resin composition. For the building trades, the extrusion equipment can produce window sills, door frames, door jams, etc. Conventional wrapping and forming equipment can produce armor coating which is fireproof, weatherproof, and chemically resistant for use on insulated hot water pipes and insulated cold water pipes. A number of techniques may be employed for applying the resin to pipe. Thus, a pipe length may be wrapped with a Fiberglas sheet which is saturated with the resin. By rotating the pipe over a continuous feed line of saturated glass mat or cloth, a carefully controlled layer of reinforced resin composition is applied to the pipe. Moreover, conventional spray guns may be employed for spraying chopped glass fibers and resin mixture onto a rotating pipe. When the coating on the rotating pipe becomes firm, the coating may be cured either in air or in an oven. A further pipe coating technique that may be used to advantage involves wrapping the pipe with Fiberglas filaments, mat, or cloth, and, hereafter rotating the covered pipe on a roller which is saturated with the resin composition of this invention. The composition of the present invention may be sprayed or coated onto a variety of surfaces, including a revolving length of pipe or flat surfaces. The interior surfaces of pipes may also be conveniently coated with the present composition by depositing a predetermined amount of resin and cement mixture on a rapidly revolving pipe. The centrifugal force of the pipe spreads the resin mixture on the interior surface and permits curing to a hard resistant, fireproof coating. Conventional equipment listed for continuous extrusion may be used with resin composition of this invention in the continuous production of gutters, downspouts and flashings. Extrusion is known in the resin forming arts as the pulling of resin shapes through extrusion dies by external means, as opposed to pushing in extrusion processes. Additionally, the resin composition may be used with conventional low pressure molding equipment in the production of such building items as shower stalls and floor pans for shower stalls. The composition of the invention may be used with conventional spray and color coating equipment to produce monolithic roofing and skins for insulation. The non-burning characteristics of the resin adds greatly to the utility of the resin in this regard. Waterproofing coatings on porous plaster and rigid wall surfaces is also contemplated with the resin composition. Conventional pressure molding equipment may be used in the manufacture of auto bodies and truck cabs, lining glass fibers impregnated with the resin composition. Because of the high thermal resistance and non-burning characteristics of the resin composition, products produced with this resin can be heated to temperatures enabling the use of heat baked enamels. Thus, products can be coated with vitrified melt finishes either over bodies molded of the resin composition or coated with the resin composition. It is also possible to foam the resin of the instant invention whereby a self-contained hard outer skin is formed. The

resultant product is a fire resistant foam. Conventional Freon may be used in an amount between about 3% to 5% to form a product having a density between about 4 to 40 pounds per cubic foot. The variation in density may be obtained by using different fillers. For example, calcium carboxylate may be used to produce a denser product than in the case where cottonseed flour is used by pumping Freon into a resin-cement composition using standard mixing equipment for producing polyurethane foams. In this case, the Freon may be injected through the low pressure tube used for catalyst injection. It is believed that the cement additive is responsible for the hard impervious smooth skin which results when the composition is foamed or expanded. The resin is particularly well adapted for use with glass fibers. When so used, the resultant product may be heated to the point at which aluminum melts without having any disintegration of the resin-glass fiber combination. In contrast, polyester resin-glass fiber combinations disintegrate and burn at relatively low temperatures, such as 300° F. The table is illustrative of the thermal stability of glass fiber-resin laminates produced by the present invention. TABLE 75°-450°: No degradation 500°-600°: Slight surface char 600°-750°: (a) No smoke (b) Unpleasant odor similar to the thermal decomposition of phenolic or formaldehyde resins (c) Char increasing slightly (d) No softening 750°-800°: (a) Penetration of char increasing significantly (b) No flame or smoke (c) Some softening (d) Pungent odor still noticeable 800°-825°: Sample first to red heat-decomposition and charring proceeded quickly from this point 825°-850°: 1/2 of sample to red heat-decomposition and charring proceeded quickly from this point 850°-900°: (a) 3/4 of sample to red heat still some structural stability exists (b) Odor alone 900°-950°: Sample entirely to red heat -ross v, arpin- 950°-1000°: (a) Sample quite soft and pliable. Resin destruction complete Notes (a) 62% of the laminated material was lost upon treatment to 1,000° F. This was accomplished with the complete absence of any type of self-supporting flame and/or smoke problem. (b) The odor was due to the decomposition of the organic constituents. The materials tested for the table were glass fiber laminates impregnated with phenol-modified resorcinol-formaldehyde resin containing 4% of a type portland cement. The glass fibers were in the form of chopped rovings in one sample and in the form of glass cloth in a second sample forming the basis of the best results of the test. While I do not wish to be bound to any particular theory I believe that the hydroxy groups of the resorcinol or other polyhydric phenolic compound react with the portland cement which, in turn, is set by the water present in the resorcinol resin system. Such a small quantity of cement is present that no appreciable heat is produced to cure the resin. In the process of hydration of the cement, the tricalcium silicate hydrolyzes, forming calcium hydroxide and a certain amount of silica gel plus dicalcium silicate. Settling occurs by crystallization of the solution formed from the hydrations products of the calcium silicates and aluminates. Gypsum is often present to prevent solution of the tricalcium aluminate which would produce high heat of hydration and flash set the cement with a resultant weak bond. EXAMPLE 1 A phenol modified resorcinol known commercially as is used as the filler. In addition, a foam may be obtained 75 Koppers "Penacolite 4122" was placed in a "Jifty" type

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32663,720 7 mixer and 4%, based on the weight of the resorcinol, Trinity white portland cement was stirred into the resin. Paraformaldehyde was then added in an amount equal to 20% of the weight of the phenol modified resorcinol. Then 20% by weight of silica flour was stirred into the mixture. Layers of glass fiber cloth were saturated and the whole molded under slight pressure at 200° F. The resulting laminate containing 60% glass fiber was strong and stiff when heated to red heat and did not burst into flame or produce smoke. The resin described above without the addition of the portland cement will not absorb the silica flour and is not sufficiently liquid to saturate the glass fibers. The glass remains dry and a solid molded product does not result. EXAMPLE 2 The procedures outlined in connection with Example I were followed except for the use of a 37% formaldehyde solution in water (formalin). Molding with glass fibers under the same conditions produced a

more flexible product than when paraformaldehyde was used. EXAMPLE 3 The procedure described above in connection with Example I was followed except that the 4% of the portland cement was mixed with paraformaldehyde instead of with the phenol modified resorcinol. By mixing the portland cement with the paraformaldehyde, reaction between the cement and resorcinol is avoided. Thereafter, the mixture of paraformaldehyde and portland cement was combined with the resorcinol and silica flour, and the mixture was molded with glass fiber as in Example 1. No difference was detected in the final result. The strength and flame-resistant properties of the final product were the same as in Example I with an added benefit of increased shelf life. EXAMPLE 4 A mixture of phenol modified resorcinol (Penacolite 4122) and 3% Trinity white portland cement were thoroughly mixed and divided into a three samples. To the first sample was added 10% cottonseed hull flour. To the second sample, 20% cottonseed hull flour was added. To the third sample, 30% cottonseed hull flour was added. Paraformaldehyde was added in an amount equal to 20% of the weight of the phenol modified resorcinol. The three samples were then molded into solid blocks and cured at 200° F. The three blocks were nearly identical in appearance and properties and differed primarily in the density of the solid product. None of the three samples would burn with a match held to it. EXAMPLE 5 The composition described in Example I for impregnating glass fibers was used in this example without the cloth. The composition, including the silica flour filler, was placed between two sheets of "Mylar" polyester film, 2 mils thick. Air bubbles were mechanically removed from under the Mylar film and the sandwich of film and resin composition was pulled through a warmed mold. Initially, the sandwich was placed on the mold until the resin composition hardened. Thereafter, the hardened portion of the sandwich was pulled through the mold, which was maintained at about 200° F., so that the soft sandwich part progressed through the mold and hardened. The Mylar film was readily stripped from the hardened composition and a strong, fireproof resin product was obtained. EXAMPLE 6 A sheet of molded glass fibers impregnated with the resin composition according to the procedure described in Example I was employed as the starting material in this example. The sheet was coated with an alkyd primer and baked at 400° F. to cure the primer coating. Then, a baked enamel alkyd finish coating was sprayed on the primed sheet and the twice-coated sheet was placed in an oven and heated by means of infrared lamps at a temperature of 450° F. The resultant product had a smooth baked enamel finish over the glass fiber sheet. This example illustrates that auto bodies and appliances may conveniently be coated with conventional high temperature baked alkyd systems. EXAMPLE 7 A phenol modified resorcinol resin (Penacolite 4122) was mixed with 4% Trinity white and 20% paraformaldehyde as in Example 1. 20% silica flour was also added and mixed thoroughly into the composition. Then 3 1/2 % Freon 118 was introduced into the mixture. The whole mass was poured into a mold and heated to about 100° F. The foam expanded and hardened within five minutes with an exotherm temperature of 150° F. was reached. A very strong foam of 20-pound density was produced which had a smooth surface on both the exposed surface and on the mold surface. The resin composition of the present invention is safe and convenient to handle because no toxic chemicals are involved, no burnable components need be present, and the composition cures at room temperature. The high strength of the resin composition is retained even to extremely high temperatures, whereby the resin composition may be used in many applications where plastic materials could not previously be used. CLAIMS: 1. An article of manufacture comprising a substrate coated with a condensation product of a polyhydric phenolic compound and an aldehyde containing between 2 and 6% based on the weight of the condensation product of hydraulic cement. 2. In a method of coating fire-proof articles made of glass fibres, comprising the steps of placing glass fibres in the desired configuration, impregnating the fibres with a composition comprising a condensation product of a polyhydric phenolic compound and an aldehyde and between 2% and 6%, based on the weight of the condensation product, of hydraulic cement, and thereafter curing to produce a shaped fibreglass article. 3. In a method of coating a substrate, the steps of applying a first coating comprising a condensation product of a polyhydric phenolic compound and an aldehyde containing between 2% and 6%, based on the weight of the condensation

product, of hydraulic cement, curing said first coating, and thereafter applying an enamel alkyd second coating. References Cited 60 UNITED STATES PATENTS 2,653,891 9/1953 Gentle et al. --- 117-161 L X 3,216,966 9/1964 Collins ----- 106-90 X ALFRED L. LEAVITT, Primary Examiner 65 C. K. WEIFFENBACH, Assistant Examiner U.S. Cl. X.R. 106-15 FP, 90; 117-126 GQ, 126 GB, 126 GF, 137, 70 161 L; 260-38

Full	Title	Citation	Front	Review	Classification	Date	Reference	Abstract	Claims	Keywords	Draw. De
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5. Document ID: US 3477881 A

L2: Entry 5 of 15

File: USOC

Nov 11, 1969

DOCUMENT-IDENTIFIER: US 3477881 A

TITLE: PROCESS FOR THE FORMATION OF ELECTRIC INSULATING COATING ON ELECTRIC IRON SHEET

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31477,881 5 of coating can be further increased. The addition amount of boric acid is preferably below 8% since if it is above 8%, it is difficult to maintain the boric acid in the dissolved state in the aqueous solution. In the above mentioned embodiment of the process of this invention, the temperature range of the iron sheet for forming coating is narrow but the upper limit of the heating condition can be extended to about 500' C. by adding a small amount of the phosphorus compound. In fact, if the coating containing no phosphorus compounds is heated to above 300' C. the organic components in the surface coating of the electric iron sheet are decomposed but the decomposition can be prevented by the addition of phosphoric acid, calcium dihydrogen phosphate, hypophosphoric acid, etc. Among them, calcium dihydrogen phosphate is comparatively inexpensive and very effective for increasing heat resistance. However, even in this case, if the coating is heated to above 500' C., the objective coating can not be formed. Of course, even though a small amount of phosphoric acid is added in an aqueous solution containing only chromium trioxide and the metal oxide and containing no organic compounds as mentioned above, the coating formed by heating the coating - at about 200' C. in the surface temperature of the iron sheet is water-soluble. That is, the addition of phosphoric acid is effective only in the case where the abovementioned organic compound is contained in the aqueous solution or coating solution. The content of phosphoric acid is, however, preferably below 5% since the addition of 5-20% of phosphoric acid has no more effects for enlarging the temperature range of iron sheet, though a good film is produced thereby, and on the contrary, reduces heat resistance and weldability of coating. If the surface of an iron sheet is clear and the coating solution can be applied uniformly, there are no problems, but if wetting property for coating is bad, the addition of a surface active agent is preferable. The addition amount of such a surface active agent is preferably below 0.5%, that is, even if it is added in an amount more than 0.5%, no more improvement in the wetting property is not obtained or, on the contrary, foaming may be formed, which reduces the appearance of coating. As the surface active agent for the purpose in the process of this invention, nonionic surface active agents of polyethylene glycol series are suitable. The following is other embodiment of the process of this invention wherein the above-mentioned additional materials are incorporated. EXAMPLE 2 Chromium trioxide ----- g-- 10 Magnesium oxide ----- g-- 2 Adipic acid ----- g-- 4 Boric acid ----- g-- 1 Surface active agent (polyethylene glycol latiryl ether) ----- g-- 0.1 Water ----- cc-- 100 An aqueous solution consisting of the above materials was applied uniformly and thinly on the surfaces of an iron sheets

h

e b

b g e e e f

e c c

e c

ec

and the sheets were heated in a furnace of 500° C. for various periods of time to form coatings. The iron sheets were immersed in boiling water for 5 minutes and the proportions of dissolved Cr+6 were analyzed quantitatively, the results of which are shown in FIG. 1 and the temperatures of the iron sheets in this case are shown in FIG. 2. As is clear from FIG. 1, there is a range wherein the temperature range for the surface temperature of iron sheet is narrow but the proportion of dissolved Cr+6 is extremely low. This is considered to be attributed to the formation of stable compounds by the reaction of ions (HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, etc.) formed by the resolution of chromium trioxide with adipic acid and Mg^{2+} on the surface of the iron sheet. Hence, the advantage of this invention is in a point that the compounds cause reaction at a comparatively low temperature to form stable coating. In Example 2, extremely stable compounds are formed when the system is heated in a temperature range of 190-270° C. in sheet temperature, but if the sheet temperature is further increased, the proportion of Cr+6 dissolved in water form coating is increased. This is because the organic compounds are decomposed by heat and the inorganic materials the bonds of which with the 10 organic materials have been cut are dissolved in water. The chromium compounds the bonds of which with the organic materials have been cut show water-solubility but when the temperature is further increased, Cr+6 is converted into Cr+3, which results in forming water-soluble coating. Such coating shows heat resistance as well as layer-boundary resistance even after annealing for relieving strains. The same behavior as in the above example was shown, when replacing adipic acid by any other compound belonging to saturated dicarboxylic acids having at least 4 carbon atoms such as succinic acid, glutaric acid and pimelic acid. In general, if the addition amount of such organic compounds is small, lustrous black-brown coating is obtained and if the addition amount is large, greenish transparent coating is obtained. By using BaO , SrO , BaO , CuO and CdO instead of using MgO or CaO , almost same results as in the examples can be also obtained. In addition the use of the hydroxides of these metals or alkaline earth metals caused, of course, the same results but by using NaOH or KOH , water-insoluble coating cannot be formed. These results show that the ions in the solutions, such as, Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Al^{3+} etc., contribute to the stability of coating but the ions, such as, Na^+ and K^+ do not contribute to the stability of coating. Even when using an aqueous solution containing only a water-soluble Cr+6 compound such as chromium trioxide and the water-soluble saturated dicarboxylic acid having at least 4 carbon atoms, coating can be obtained, but indicating a peculiar winding curve as shown in FIG. 1, which is considered to be caused by the action of iron ions formed from the electric iron sheet to the formation of coating. When the pH of the aqueous solution containing only chromium trioxide and the water-soluble dicarboxylic acid having at least 4 carbon atoms is kept to about 5-6 by adding NaOH or KOH into the solution, water-insoluble coating can not be obtained. This is because Na^+ ion or K^+ ion does not contribute to the stability of coating and also the surface of the electric iron sheet is hardly attacked by the coating solution since the pH of the solution is increased. The formation of coating from an aqueous solution containing only MgO and Cr_2O_3 needs a high temperature treatment, which is substantially different from the process of this invention, in which the low-temperature treatment is one of the main features. Moreover, in the process of this invention, it is unnecessary to carry out the heating process in a reducing atmosphere. Further, the compounding ratio of Cr_2O_3 to the bivalent metal ions as of Mg , Cd , Be , Ba , Sr , Ca , Cu , etc. in this invention is not restricted to a definite one. For example, if the mixing ratio of MgO and Cr_2O_3 is 1:2 mole ratio or 1:4 mole ratio, the same curve as in FIG. 1 can be obtained. The reaction rate of the aqueous solution of chromium trioxide and the organic compound is influenced generally by the pH value of the solution, and the oxidation reaction of the organic compound proceeds quickly and precipitates are easily formed as the pH is decreased. When, for example, an alkaline earth metal oxide is added into the aqueous solution of chromium trioxide, the pH of the solution is increased, the oxidation reaction of the organic compounds in the aqueous solution becomes slow, the formation of precipitates becomes difficult.

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7 cult. For example, in the case of Example 2, the pH of the solution is 6.5 and the solution is very stable without forming precipitates but in this case, if MgO is not added in the system, the pH is 0.4 and precipitates are easily formed, which makes the continuous coating procedure difficult. In general, in the case of using a carboxylic acid as the organic compound, the prepared solution is stable without influence with the pH but in the case of using the alcohols or sugar, the solution is unstable if the pH value is low, hence it is preferable in stability of solution to carry out the coating at a pH higher than 3. However, it should be understood that the coating process of this invention can be conducted even at the pH lower than 3. The coating formed by the coating solution in Example I shows lustrous yellow brown. As the results of experiments, it was confirmed that the coating was not infected by a transformer oil, trichloroethylene, and Freon gas. The coating obtained in Example I had a good adhesive property, that is, when the iron sheet was bent to an angle of 180° along a rod of 10 mm. in diameter, no stripping phenomena occurred. The coating had an excellent rust resistance. The results of measuring the layer-boundary resistance by Method 2 in ASTM are as follows: Ohm-sq. cm./sheet

No. 1	-----	209	No. 2	-----
-----	123	The layer-boundary resistances of coatings after subsection to annealing for relievin.- strain for 4 hours at 800° C. in an atmosphere of hydrogen 10% and nitro.-en 90% are as follows, which are superior to conventional phosphate-containing coatings: Ohm-sq. cm./sheet		
No. 1	-----	85.7	No. 2	-----
-----	58.1	The space factor of the electric iron sheets before and after the formation of coatings are as follows:		
Be,fore	After	No. 1	-----	97. 3 96. 8
No. 2	-----	97.0	96. 5	

Two hundred (200) electric iron sheets of 50 x 100 x 0.5 m./m. were piled and after welding the side surface with 8 beads, a shearing test is applied to measure the streng',h of the welded portion. The results are as follows, which show the excellence of strength. For reference, a test result about an iron-phosphate coating is shown together. Max. shearing load, kg. Iron By the phosphate inventioii

coating No. 1	-----	3,900	3, 500	No. 2	-----	4,000	2, 500
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Having thus described the invention, what is claimed is: 1. A process for the formation of an electric insulating coating on an electric iron sheet, comprising the steps of applying on the surface of an electric iron sheet a reducing solution consisting essentially of 0.5-20% of hexavalent chromium ion and 0.3-8% of at least a bivalent metal ion selected from the group consisting of copper ion, cadmium ion, and alkaline earth metal ion, said reducing solution having been further added with 0.1-8 % of a water-soluble saturated aliphatic dicarboxylic acid reducing agent having at least 4 carbon atoms and 32477)881 8 having a miscibility of above 15 minutes with at least one of these ions at room temperature, and heating it for 10-18,0 seconds to 150-300° C. 2. A process for the formation of an electric insulating coating on an electric iron sheet, comprising the steps of applying on the surface of an electric iron sheet an aqueous solution consisting essentially of 0.5- 20% of hexa:valent chromium ion, 1-5% of at least one of bivalent alkaline earth metal ions, and 0.1-20% of phos- 10 -phoric acid ion, said aqueoi-is so!ution having been furth-,r added with 0.1-8% of water-soluble saturated aliphatic dicarboxylic acid reducing agent having at least 4 carbon atoms and having a miscibility of above 15 minutes with at least one of these ions at room tempera- 15 ture, and heating it for 10-180 seconds to 150-500° C. 3. A process for the formation of an electric insulating coating on an electric iron sheet, comprising the steps of applying on the surface of an electric iron sheet an aqueous solution consisting essentially of 2.5-10% of 20 hexavalent chromium ion and 1-5% of at least a member selected from the group consisting of copper ion, calcium ion, magnesium ion and barium ion, said aqueous solution having been further added with 0.1-8% of at least a member selected from the group consisting of succinic 25 acid, glutaric acid, adipic acid and pimelic acid and heating it for 15-30 seconds at 250-280° C. 4. A process for the formation of an electric insulating coating on an electric iron sheet, comprising the steps of applying an aqueous solution consisting essentially of 30 2.5-10% of hexavalent chromilim ion and 1-5% of at

least a member selected from the group consistin.- of copper ion, calcium ion, magnesium ion and barium ion, said aqueous solution having been further added with 0.1-8% of at least a member selected from the group 35 consisting of succinic acid, glutaric acid, adipic acid and pimelic acid and 0.01-0.5% of a nonionic surface active a.-ent of polyethylene glycol series, and 1-8% of boric acid and heating it for 10-180 seconds to temperatures of 150-300' C. 40 5. A process for the formation of an electric insulating coating on an electric iron sheet, comprising the steps of applying on the surface of the electric iron sheet an aqueous solution consisting essentially of 2.5-10% of hexavalent chromium ion and 1-5% of at least a mem- 45 ber selected from the group consisting of copper ion, calcium ion, magnesium ion and barium ion, said aqueous solution having been further added with 0.1-8% of at least a member selected from the group consisting of succinic acid, glutaric acid, adipic acid, and pimelic acid 50 and 0.1% of a nonionic Surface active agent of polyethylene glycol series, and 2- 5% of boric acid, and 0.1-20.0% of phosphoric acid, and heating it for 10-180 seconds in a ten-lperature range of 150-500' C. 55 References Cited UNITED STATES PATENTS 2,472,592 6/1949 Kiefer -----
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 Primary Examiner U.S. Cl. X.R. 70 148-113

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KMIC	Draw De
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6. Document ID: US 3383225 A

L2: Entry 6 of 15

File: USOC

May 14, 1968

DOCUMENT-IDENTIFIER: US 3383225 A

TITLE: Acid-resistant enamels

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3)383)225 5 use. To gain satisfactory metal adherence, T may employ any adherence promoting oxide, or mixtures thereof, up to the total amount of 5 mol percent of the total composition. CdO, performing a distinctly different primary function (i.e., that of dissolving TiO₂) in my compositions, may additionally be present within the percent amount specified for that oxide in my compositions independently of the presence or abser.,ce of any other adherence promoters. Suitable adherence promoters are CuO, NiO, CoO, Sb₂O₃, PbO, Bi₂O₃ and mixtures thereof. With the exception of Sb₂O₃, which like CdO also performs another desired function in my frit compositions, these various adherence promoters may be employed in amounts up to 5 mol percent. Not more than about 1 mol percent of Sb₂O₃ should be employed because this oxide causes a loss of gloss in the resulting enamel. For this reason Sb₂O₃ is preferably, but not necessarily, employed with small amounts of another adherence promoter or with CdO present. By varying the amounts of CoO, CuO and NiO in the frit, various colors from deep-blue to blue to blue-green can be obtained in the frit and thus in the enamel coating. Sb₂O₃, PbO and Bi₂O₃ as adherence promoters permit the formation of colorless coats. PbO, of course, is generally not preferred as a constituent because it is a toxic material. To prepare my glass enamel frits, raw batch materials, e.g., CaCO₃, CaF₂, TiO₂, etc., mixed in amounts calculated to give the mol percent analysis hereinbefore discussed, are melted together at a temperature range of about 1000' C. to 1200' C., and then quenched in water and dried. For exaniple, a preferred frit composition having the analysis of Example 10 may be prepared by mixing 15.6 parts by weight of TiO₂, 1 part ZnO, 4.6

parts BaCO₃, 3 parts CdO, 6.7 parts Li₂CO₃, 7.7 parts of Na₂PI0031, 19.4 parts Na₂CO₃, 11.9 parts K₂CO₃, 1 part NaF, 22.7 parts SiO₂ and 6.4 parts H₃BO₃. After thoroughly mixing these materials, they are melted in a refractory vessel, such as an alumina-silicate vessel, at a furnace temperature of approximately 1100° C. The mass is heated until it melts down to a homogeneous fluid state, and then is quenched in water, which action shatters the glass into small particles. The frit is then dried and is ready for use in a slip formulation for enameling. Slip formulations may be prepared by combining the frit hereof with water and suitable suspending and/or binding agents, i.e., sodium silicate, borax, etc., and then grinding the mixture to suitable fineness for smooth application to clean surfaces. To the slip formula may also be added coloring oxides, e.g., cobalt aluminate blue, nickel chromate green, etc., up to an amount of about 10% by weight of the slip formulation, if desired. Also, if desired, opacifying oxides such as SnO₂, ZrO₂, TiO₂, etc., may be additionally added up to an amount of about 15% by weight of the slip formula. Small amounts of mill additives such as potassium dichromate may be desirably used to improve the surface appearance of fired enamel coatings, i.e., to provide coatings essentially free of pinholes and of improved tear and chip resistance. Slip formulations vary greatly and by using different formulations it is possible to vary somewhat the properties of a resulting enamel. One illustrative slip formulation is as follows: 100 parts of frit, 3.36 parts of potassium silicate powder (28.3% K₂O and 70.7% SiO₂), 2.12 parts of KOH, 2.53 parts of H₃BO₃ and 50 cc. of water. Another is: 100 parts of frit, 9.1 parts of sodium silicate solution (8.9% Na₂O, 28.7% SiO₂, and 62.4% water), 5 parts of K₂B₄O₇·5H₂O, 1.8 parts of KOH, and 50 cc. of water. A third is: 100 parts of frit, 4 parts of a watersoluble crushed glass mixture formed of 9.3% Na₂O, 34.7% K₂O, 25.5% B₂O₃, and 30.5% SiO₂, and 50 cc. of water. All three of these aforementioned slip formulations have been employed with my enamels with very successful results. The following merely illustrates a further preferred slip formulation, as well as a suitable procedure for enamel-6ing: 100 grams of the frit of Example 10 were mixed in a ball mill with 2 grams of anhydrous borax, 1 gram of KOH, 3 grams of sodium metasilicate (21.8% Na₂O, 21.1% SiO₂, 57.1% H₂O), and 50 cc. of water. (This particular slip formulation was used in making all specimen enameled panels for testing according to the acid resistance and alkali resistance tests described below.) The mixture was ground until the residue, after screening on a 325 mesh screen, was less than 1 gram per 50 cc. of slip. An aluminum alloy panel was cleaned by washing with carbon tetrachloride, dried, and sprayed with a sufficient amount of the slip to give a coating weight of 0.3 gram of enamel per square inch. Other methods of applying the slip to the panel are also suitable, methods such as dipping and electrostatic spraying included. The coated panel was then air dried to remove water and the piece fired at 520° C. for 10 minutes, resulting in the formation of a porcelain enamel coating free of surface defects such as for example pinholes, and possessing a high gloss, a high degree of adherence and a white semi-opaque color. Aluminum alloy panels that contain large amounts of silicon, magnesium, etc., in the alloy are sometimes difficult to enamel unless a suitable oxide surface for enameling is first prepared. A suitable preliminary treating procedure for such panels is as follows: first clean organic matter from the panel by a soak period of about 3 to 4 minutes in trichloroethylene. Then dip the panel for about 2 minutes in a 5% sodium hydroxide solution held at about 180° F. Next rinse the panel thoroughly with water and dip it for about 2 minutes in a 30% nitric acid solution held at about 180° F. Following this, again rinse the panel in hot water and immerse it for about 10 minutes in boiling water. Then dip it for about 2 minutes in a 5% potassium chromate solution held at about 180° F. 35 or higher. Finally rinse the panel thoroughly and allow it to dry. The resulting cleaned panel may be enameled without difficulty according to well known procedures such as described above. While primarily designed for application to aluminum-type surfaces, my enamels are also useful in coating such material as copper and silver. The relatively high dielectric constant of my enamel may render it particularly useful in the electrical industry. In Tables I, II and III, various illustrative examples of this invention are set forth in terms of the molar percent analysis of inorganic constituents as calculated from the raw batch.

Examples 5 through 10, inclusive, 12 through 24 inclusive, and 30, illustrate preferred frit compositions hereof. In the row labeled "Acid test" are set forth the measured weight losses resulting from an acid resistance test which involves refluxing 25 ml. of boiling (100° C.) 6% citric acid (by weight) in contact with a 1" square area of an enameled panel having a coating weight of enamel 55 of about .3 gram per square inch (which weight is well above the average coating weight employed commercially) for 21/2 hours. (Of course, a larger area and proportionately larger quantity of 6% citric acid, etc., may be used in conducting the test; and thereafter, appropriate calculation made to reduce results to the standard herein set forth.) Specifically, in conducting the test, an enameled panel of adequate size is placed, enamel face upward, on a steel plate over a heating element. Over the enamel coating is rigged a bell jar (a jar having a narrow throat opening above and having its bottom removed) having a one square inch total open bottom area. A sealing gasket also having an opening of one square inch in total area is interposed between the enamel surface and the bottom edge of the bell jar. 25 ml. of hot 6% citric acid solution is then charged into the bell jar, a reflux condenser is fitted over the throat opening of the jar, and boiling of the citric acid solution at 100° C. continued for 21/2 hours. The enameled panel is weighed before and after the boiling acid treatment and the weight loss caused by the treatment is a rather accurate indication of what acid resistance

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3) 3832225 7 the enamel coating will exhibit in practical uses. It also is a rather accurate indication of the weather resistance of the enamel. In order for an enamel to be suitable for decorative exterior use on kitchenware, it should have an acid resistance, as measured according to the foregoing boiling citric acid test, exhibiting only a low weight loss of not more than about 0.03 gram per square inch. Porcelain enamel coats made using the preferred enamel frit compositions hereof can satisfy this requirement, and in addition, satisfy 10 other requirements for aluminum-type enamels. To my knowledge no prior art alkali-titania-silicate enamel is suitable for such decorative use on aluminum type kitchenware. None known to me possesses sufficient resistance to acid attack in combination with other required properties. The row labeled "Alkali test" contains the weight losses of the enamels according to an alkali resistance test consisting of refluxing 25 ml. of a boiling (100° C.) solution of 5% hydrated sodium pyrophosphate (Na₄P₂O₇ · 10H₂O) by weight, in contact for 21/2 hours with a one inch square enameled specimen panel, using the technique otherwise described for the acid resistance test above. Enamels all exhibit a high alkali resistance, according to this test, and in fact, exhibit weight losses less than about 0.05 gram per square inch of enameled panel. For preferred compositions, the alkali weight loss is less than about 0.03 gram per square inch of panel. This high alkali resistance is particularly noteworthy when it is found in combination with a high acid resistance, as it is in the case of the enamels taught herein. The procedures followed for the "Acid test" and "Alkali test" herein set forth give results substantially the same as those obtained using procedures outlined in Commercial Standard CS100-47, recommended to industry in June of 1956 by the Quality Development Sub-Committee of the Aluminum Division, Porcelain Enamel Institute, Inc. as a tentative standard for evaluating the quality of porcelain enamel on aluminum. Approximate maturing temperatures in degrees centigrade and coefficients of thermal expansion per ° C. from 50 to 350° C. are set forth for each glass frit. Additionally certain ratios between ingredients for each composition are set forth in the tables. TABLE I Ex. No. -----

-----	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
-----	34	30	30	30	42.1	40.7	38	34.4	43.0	13	TiO	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
-----	21	16	16	16	12.7	17.1	21	17.7	13.0	17	Total	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
-----	55	46	46	46	54.8	57.8	59	52.1	56.0	50	CdO	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
-----	3	3	3	3	3.4	2.5	3	1.6	1.5	2	ZnO	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
-----	3	3	3	3	2.0	2.5	3	1.1	2	1	B ₂ O ₃	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
-----	3	-----	-----	-----	-----	-----	-----	2.5	2.8	3	2.1	2.5	2	SrO	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----

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----- 3 C"lo -----
----- 3 INIgo -----
----- 3----- Total C, roup II -----
----- 99997. 97. 89 4.8 6.05 Li@O -----
----- 10 13 13 13 6.4 8.5 10 8.3 6.5 8 1@20 -----
----- 4 6 6 (; 4.9 5.3 4 7.8 5.0 7. r) Na,O -----
----- 16 20 2( 20 38.6 17.6 16 20.8 I'). 0 2() N,iF -----
----- 2.0 ----- @. 02 Total --
----- 3o 39 39 39 31.9 31.4 30 36.9 32.5 37.5 13203 -----
----- 6 4 4 4 3.4 3.0 2 3.1 3.5 4.5 P205 -
----- 2 2 2 2.0 ----- 3.1 2 3
Total ----- 66665.4 3.0 2 6.2 5.5 7.5 Itztitio
SiO2/TiO2 ----- 1.62 1.88 1.88 1.88 3.31 2.38 1.88 1.
(@)4 3.31 1.94 Itiitio TiO2/Tot-,il Grotii) 11 ----- 2.33 1.78
1.78 1.78 1. 61 2.19 2.33 3.69 2.17 3.4 Ratio TiO2+SiO2/Totaf C@roup II -----
----- 6.11 6.11 5.11 5.11 6.94 7.41 5.57 10.86 9.3 10. 0 Acid test -----
----- -037 .047 .031 .033 .009 .018 .027 .021 .007 .024 Alkali
test -----
034 .048 .034 .036 .029 .016 .014 .020 .010 .025 a -----
----- 560 530 550 540 560 540 560 540 560 520 -----
----- 15.0 16.3 15. 114.8 14.3 14. 615.1 15.4 14. 716. 1 See footnotes
at ciid of Table III. TABLE H Ex. No -----
11 12 13 14151617181920 sio2 ----- 36.2
38.0 34.4 42.134.433.734.433.735.642.5 TiO2 -----
----- 14.7 15.4 17.7 12.717.717.317.717.315.812.8 Total -----
----- 50.9 53.4 52.1 54.852.151.052.151.051.456.3 SnO2 -----
----- 2.9 3.0 -----
CdO ----- 1 2 --- i --i --- i ----- 1 2 ZnO -----
----- i. fi BaO -----
----- 2.1 2.5 2.1 2.1 2.1 2.1 2 2.5 SrO -----
----- .6 .6 Total Group II -----
----- 2.3 2.43.2 4.53.23.13.23.1 4 6.5 Li2O -----
----- 7.2 7.58.3 6.48.3 8.28.38.2 6.9 6.4 K2O -----
----- 7.6 7.97.8 4.07.87 .77.87.7 7.9 4.9 NO2O -----
----- 17.1 18.020.818.6 20.820.420.820.4 18.8 18.8 NaF -----
----- 2 4 2 Total -----
----- 31.9 33.4 36.9 31.9 36.9 36.3 36.9 36.3 37.6 32.1 B203 -----
----- 11.0 6.7 3.1 3.4 3.1 3.0 3.1 3.0 4 3.4 P206 -----
----- 1.0 1.1 3.1 2 3.1 3.0 3.1 3.0 2 2 Total -----
----- 12.0 7.8 6.2 5.4 6.2 6.0 6.2 6.065.4 ctio -----
----- 1.6 3.4 Nio -----
----- 1.6 3.6 -----
----- coo 1. C, 3. C - ----- SI)203 .7 Total -----
----- 1.6 3.4 1.6 3.6 1.6 3.61.7

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Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KWMC	Draw De
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7. Document ID: US 3284354 A

L2: Entry 7 of 15

File: USOC

Nov 8, 1966

DOCUMENT-IDENTIFIER: US 3284354 A

TITLE: Reaction product of metal dithiophosphate, polyamine and alkenyl succinic acid or anhydride

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Utilited States Patent Office 3,284,354 3,284,354 REACTION PRODUCT OF METAL DITHIOPHOSPHATE, POLYAMINE AND ALKENYL SUCCINIC ACID OR ANHYDRIDE Norman Tunkel, Perth Amboy, and Hqrold N. Miller, PlaiBfield, N.J., assignors to Esso Research and Engineering Comrany, a corporation of Delaw-tre No Drawing. Filed Dec. 12, 1963, Ser. No. 329,955 8 Claims. (Cl. 252-32.7) This invention relates to a product obtained by reacting metal dithiophosphate with polyamine to form an adduct, which adduct can be further rea6ted with alkenylsuccinic anhydride to form a condensation product, methods of preparing said product, and hydrocarbon and lubricating oil comr)ositions which contain said product. Recently, various nitrogen-containidg derivatives of high molecular weight alkenylsuceinic anhydride have become known as sludge dispersants, particularly for lubricating oils. Several of these derivatives are described in U.S. Patents 3,018,247; 3,018,250 and 3,018,291. A particularly effective derivative of this general type can be prepared by condensin- alkenylsuceinic anhydride with a polyamine, e.g., tetraethylene pentarnine, as described in Australian patent application No. 63,803 filed A@uguSt 22, 1960. It was further taught in this Australian patent that a combination of metal dithiophosphate with the condensation product of alkenylsuccinic anhydride and tetra ethylene pentamine, showed syncrgy with regard to sludge handling ability and maintaining engine cleanliness. it has now been found that by first reacting polyamine with metal dithiophosphate to form an adduct, and then further reacting this adduct with alkenylsuccinic anhydride thit a single additive material is formed having superio, sludge handling ability than said synergistic combination taught by said Australian patent. Polyamine reactants for the formation of the adduct prodlict of the invention include those of the general formula: $N1-1, (C1-1,) n[NH(CH2), J,, i-NI-12$ where ii is I to 5, preferably 2 or 3, and m is 0 to 10, preferably 0 to 4. Specific exaniples of such polyamines include ethylene diamine, diethylene triamine, tr;cthylene tetraamine, tetraethylene pentamine, octaethylene nonamine, propylene di,,imine, tetrapropylene pedtamine, etc. Also included are N-alkylpi- peilazines of the forriiula: $CH2'-CH2\ 1-12-NT-cHz-OH2-N/\ N-P@ CH@-CH2$ where R is selected from the group consisting of hydro- gen, $-CH2-CH2-NH2$ and $-CH2CI-1, NH-CI-I, -CH, --NH2$ Met.il dithiophosphates reacted with the polyamine to form the adduct include those of the -,Cneral formula: $R-0\ s\ p\ @5\ SI-1ki\ IRI-0$ wherei-ii ii is the valence of M. R and R' are the same or different radicals of I to 30, preferably 2 to 12, carbon atoms each, including radicals stich as aryl, alkyl, aralkyl, cycloalkyl, aryloxyalkyl, acylaryl and alkoxyaryl radicals. Preferably, R and R' are hydrocarbon -roups and generally will be alkyl groups of 3 to 8 carbon atoms. Usually, the total number of carbon atoms in R and R' will be sufficient that the dithiophosphate per se is soluble in mineral lubricating oil. M can be a metal capable of coordination with amines of Groups 11-A to V-A, I-B to VII-B and Group VIII of the Periodic Table described on Patented Nov. 8, 1966 2 pages 308-309 of Handbook of Chemistry and Physics, 26th ed., published by Chemical Rubber Publishing Co. of Cleveland, Ohio. Examples of such dithiophosphates include nickel di(2,4- diamyl phenoxyethyl) dithiophos- phatc; aluminum tri(lauryl phenyl) dithiophosphate; zinc di(methoxyphenol) dithiophosphate; zinc di(amyl) dithiophosphate; cadmium di(dicapryl) dithiophosphate; zinc di(lauryl) dithiophosphate; zinc amyl-butyl dithiophosphate, etc. 10 The polyamine and the metal dithiophosphate can be Complexed together at room temperature. A solvent is usually desirable during this complexing operation because of the larg.- increase in viscosity that generally takes place. Because of the oil-insolubility of the resulting 15 complex, solvents such as chloroform, isopropanol, methylene chloride, ether, etc. can be used for this purpose. After the complex is formed, it is then reacted with an alkenylsuccinic anhydride or the corresponding acid. However, the alkenylsuccinic anhydride will usually be 20 used since it is very readily prepared by reacting maleic anhydride with an organic compound having a double bond at one end to thereby produce an intermediate com- polind having the formula: $H\ 0\ 25\ 1\ -8\ R-C\ I-C'o\ I\ 11\ 30\ H\ 0$ wherein R is an alkenyl radical, either substituted (e.g. chlorinated or sulfurized) or unsubstituted. R will usually contain a total @of 30 to 250, preferably 60 to 120, carbon atorns. Because of its ready availability and low cost, R 35 is preferably a polymer of a C2 to C5 monooletin, having a molecular

weight of about 400 to 3000, e.g. about 700 to 2500. Examples of such monoolefins are ethylene, propylene, 1-butene, etc., with a particularly preferred monoolefin being isobutylene. 10 Particularly preferred is polyisobutenyl succinic anhydride, the preparation of which is described in U.S. Patent 3,018,250, @column 3 lines 57-71. While this reaction is conventionally carried out at atmospheric pressure it has recently been found that carrying out the reaction b'etween 4@5 maleic anhydride and polyisobutylene at about 450° F. under pressure, that the reaction time can be materially reduced, for example from a typical reaction time of 24 hours to as little as 8 hours reaction time. The reaction between the alkenylsuccinic anhydride and 5(the complex of polyamine and dithiophosphate can be carried out simply by heating the two materials together while removing the water of condensation and solve, .it, e.g. chloroform. The relative ratios of the succinic anhydride, the poly- 55 amine, and the metal dithiophosphate can be varied relative to each other over a wide range, depending partly upon the number of amine -roups present in the polyamine. A typical ratio that will give good results is obtained by reacting one mole of dithiophosphate with one 60 mole of the polyamine to give an adduct which can be further reacted with one mole of alkenylsuccinic anhydride. The resultin, .i material will provide good wear and oxidation protection and it will have good dispersancy. In general, the relative degree of dispersancy appears to be 65 related to the amount of alkenylsuccinic anhydride used, while the antiwear and oxidation stability appears to be related to the proportion of metal dithiophosphate used. Thus, the chemist by varying the amounts of dithiophosphate relative to alkenylsuccinic anhydride, can tailor- 70 make the final product to have varying degrees of dispersancy, oxidation inhibition and antiwear properties. Generally, however, within the range of about 0.5 to 2.0 moles

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3,284,354 3 of the alkenylsuccinic anhydride and about 0.2 to 4.0 moles of the metal dithiophosphate will be used per mole of the polyamine. Usually, within this range, the desired balance between antiwear and dispersancy properties will be obtained. The exact ratio of reactants is dependent, -) of course, on the number of amine groups available in the polyamine molecule. Thus, using one mole of polyamine, the total number of moles of alkenylsuccinic anhydride and dithiophosphate that are used should be no greater than the total number of amine groups present. 10 In the case of tetraethylene pentamine, having five amine groups, the total moles of dithiophosphate and alkenyl- succinic anhydride will also be five. Lubricating oil compositions for crankcase use will comprise a major proportion of lubricating oil, and 0.01 15 to 20 wt. percent, preferably 0.1 to 10 wt. percent, of the @additive of the invention as sludge dispersant, antiwear and antioxidant additive. Oil concentrates may contain 20 to 80 wt. percent of the additive. For use in fuels, such as gasoline and fuel oil, amounts of about .001 to 1.0 20 wt. percent of the additive will generally be used. The oil component of the lubricating oil compositions can be a mineral lubricatin.- oil or a synthetic lubricating oil including diesters such as di-2-ethylhexyl sebacate, complex esters, carbonate esters, polysilicones, and other 25 synthetic oils. The lubricating compositions of the invention can also include conventional lubricatin.- oil additives in amounts of 0.05 to 10.0 wt. percent, usually 0.5 to 4.0 wt. percent each, based on the wei.-ht of the total composition. For 30 example, oxidation inhibitors such as phenyl-alpha-naph-thylamine; rust inhibitors such as sodium nitrite and lail- olin; other dispersants or deter.@ent additives such as basic calcium petroleum sulfonate, phosphosulfurized polyisobutylene, and barium phenate sulfide; viscosity index im- 25 provers and pour depressants such as polymethacrylates; dyes; etc. can be used. Exan7ple I Pai-t A.- A complex of tetraethylene pentamine with 40 zinc dialkyl dithiophosphate was prepared as follows: 100 grams (.53 mole) of tetraethylene pentamine was dissolved in 160 grams of chloroform. To this chloroform solution was then added 990 grams (1.31 moles) of zinc dialkyl (amyl/isobutyl) ditliiophosphate in the form of 45 a mineral lubricating oil solution containing 75 wt. per- cent of said dithiophosphate. The dialkyl groups of this dithiophosphate consisted of about 65%

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polyisobutenyl succinic anhy-

Full	Title	Citation	Front	Review	Classification	Date	Reference	Abstract	Abstract	Claims	Keywords	Drawings
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8. Document ID: US 3197300 A

L2: Entry 8 of 15

File: USOC

Jul 27, 1965

DOCUMENT-IDENTIFIER: US 3197300 A

TITLE: Process of producing a soil nutrient by reacting a humic matter with nitric acid

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@,197,300 effective as a result of sai,lpl@i,@i- tests, as will be later described. At present, there are seen on the mark-et various types of salts of nitro humic acids such as amm@onium salt, sodium salt, calcium salt and urea salt. Compared with 5 -these salts the soil builder of the present inv@-ntion has distin,-Uishable advanta,-es brou.-ht forlh, by the process of manufacture i-n which nitro humic acid is. brought into reaction with serp.-ntine, calcined serpe- @it,@ne or oth--r silicie acids, together with siilo-Qtances containin.@ rna.g- lo nesium in macro reticular bonding therenvith, so that said ma.-nesium is combined with humic acid radicals tliereby providin.- the product with sur-h chemical properties as to be easily assimilated by the growing plant and such physical properties as to accelerate the ganulation of soil 15 particles which is esse-,itial to the ma:intena@ice of porosity, aer,ition and water-absorption. In other words, it is necessary to release the pers@,stent in,er-bonds of hii- mic acid par-ticles in humus which prevent the effective action upon soil and plant. For this purpose, the humic acid 20 particles may be disinte,-rated into monomers so as to become highly active. To increase this activity, accord- ing to the present invention, these acids are subiected to nitration. The soil improvin.- compound thus obtained excels ali 25 conventional manurin.- and fertilizing chemicals in that it is more readily and easily taken up by the so-II and the ve.-etation, @as well, and in that it possesses such a hi.- h dissolving power as consistent with the desired retentivity in the soil. Another merit worthy of note as character- 30 istic of the present invention is the fact that humic acids or nitro humic acids are made to coexist with magnesium, thereby increasin.- the index of phosphoric acid absorp- tion by the plants. Further characteristic of the present invention is that prior to its reation with a ma,-nesia-con- @35 taining material such as serpentine, nitro humic -acid is treated to become a water-soluble salt with alkali salts of the type. including Na, K, NH4 and the like, so that when it is @admixed with a powder of said niagnesia- containing material and heated to a temperature betweezi 20 and 40 120' C. to effect exchange reaction it will accelerate the precipitation of insoluble nitro humic acid-i- nagesium salts thus increasing the yield of the desired magnesium salts. Let us now observe the instance ,vhere silicic acid 45 magnesium is used as a reactant with nitro hur@iie acid. Magnesium, being silicate in this instance, will combine with carboxyl radicals of nitro humic acid but not as easily as it would react with ions in the solution. 'ne reaction rate plotted against time is graphed in the ac- 50 companying drawing. F;-G. 4 shows by the dotted line curves I ard ll and yield of nitro humic acid ma,-nesii- im obtained from the first series of experinients wherein 100 parts of nitro humic -acid obtained by the reaction of lignite w,@th nitric acid were admixed 55 with 100 parts of non-calcined serpentine, the whole being heated at tem- peratijres ranging from 80' C. to 110' C. - Subsequeit tests included the step of forming a water-soluble salt of nitro humic acid with the aid of salts of sodium, potas- sium or ammonium, followed by the suspension of fine 60 articles of silicic acid magnesium.

In this manner the two reacting components undergo an exchange reaction causing the greater proportion of insoluble nitro humic acid-silicic acid magnesium to settle successively. For example, to 100 parts nitro humic acid may be added 0.4 to 1.0 part of 5% NaOH solution and 4 to 7 parts calcined or non-calcined serpentine. The mixture may be aged at normal temperature until the precipitates are separated and identified. Experimental evidence shows that the desired product is obtainable at a yield of 70 to 90%.

This is illustrated by the solid line curve and all of the above. Such a high yield may be attributed to the fact that Na, K or NH₄ ions will, when brought into reaction with silicic acid, magnesium, become free and readily combined with unreacted nitro humic acid, thus providing a catalytic action so that net production of the desired nitro humic acid magnesium may be greatly increased. Used as a magnesium-containing material in the present invention other than calcined or non-calcined serpentine is chrome slag which is, however, less reactive than the above two; calcined serpentine being less reactive than non-calcined serpentine.

When a reaction mixture of nitro humic acid and silicic acid magnesium is subjected to aging, the yield of the desired product increases nearly in proportion to the temperature but sharply declines at elevated temperatures in excess of 120° C. where nitro humic acid is believed to undergo decomposition. In addition to the above noted characteristic features of the present invention, it may deserve particular note that the process of the invention exhibits industrial usefulness when applied to rather difficultly soluble magnesium-containing materials such as serpentine in that silicic acid contained in the material can be maintained free in the end product and the effectiveness of magnesium is thereby pronounced. Now, as a means of supporting the effectiveness of the invented soil improver the solubility in citric acid is discussed as follows. The solubility of non-calcined serpentine in citric acid is normally around 3.8% and reaches barely 7.2% after being calcined in its massive state. However, if it is reacted with nitro humic acid in accordance with the present invention the citric acid solubility increases as much as to 58% with accelerated magnesium activity as shown in Table 1.

TABLE I Solubility in Citric Acid (given in percent - age increase)	
Non-calcined serpentine	3.8
Calcined serpentine	7.2
invented product	58

The above data have been ascertained to hold true with silicic acid also. The accompanying drawing graphically illustrates the change of reactivity with operating temperatures and reaction time with respect to the case of nitro humic acid with magnesite, non-calcined serpentine and calcined serpentine. FIG. 3 depicts the case where 90 parts nitro humic acid obtained by reacting lignite with nitric acid was admixed with 5 to 15 parts magnesite. FIG. 4 shows the case where 80 parts nitro humic acid was admixed with 15 to 25 parts non-calcined or calcined serpentine, and further added with 30 to 100% of water, the whole being heated at 100 to 110° C., 80 to 90° C., and 50 to 60° C., respectively. The curves I, II and III respectively show the corresponding yields of nitro humic acid magnesium, suggesting the possibility of a theoretical 100% yield. Even with non-calcined serpentine, the reactivity was found to average 60 or 70%. Essential to the success of reaction of nitro humic acid with magnesium is the presence of water in an amount of 30 to 100% of the mass. The use of water less than the range of quantities just stated results in poor yields due to early evaporation of moisture content and hence insufficient reaction. Conversely, excessive water entails undue loss of heat. As already mentioned, the critical upper limit of reaction temperatures should be considered in the neighborhood of 120° C. for all practical purposes consistent with economy and efficiency. The present invention will be described below in connection with the continuous mode of its operation. A great many literature and technical reports have been introduced concerning the process of manufacturing nitro humic acid soil improving compounds. Most of them, however, deal exclusively with the batch type process.

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3,197,300 describes and typically contemplate employment of rather mild temperatures for the reaction of humus with nitric acid, these temperatures being controlled,

d by heating or cooling the composition using a relatively dilute nitric acid. High care is retained to maintain the critical temperature conditions necessitated, sometimes the rapid cooling of the mixture to remove excessive reaction heat. In such instances, it is quite difficult to maintain a smooth reaction because the mixture is apt to boil over in the absence of proper care. For the more, i.e., of nitro humic acid it has been required to filter and wash nitro humic acid to remove reaction waste liquor and to neutralize the precipitates suspended in water with alkali. Therefore, the industry has been seeking for a practical technique of continuously producing nitro humic acid or its salts in large quantities at low cost. To meet this requirement, the present invention comprises feed material such as lignite, peat, turf and the like in crushed form into a sealed chamber, injecting 20 to 50% nitric acid into the feed material while in transport toward the end of the chamber and agitating the whole until the desired nitro humic acid is produced. In this instance of the invention, it is to be noted that the entire steps of the process are carried out in a continuous mode of operation without having to heat the chamber from its exterior. While the above reaction is being carried out, one or more materials contained in the material chosen from the group consisting of dolomite, magnesite, magnesite, silicic acid, magnesium, magnesium hydroxide, and the like, can be added to and reacted with the initial mixture so that nitro humic acid may be obtained on a continuous basis. In an effort to achieve a smooth and effective reaction, the present invention contemplates employment of a kneader-type reactor capable of continuous operation. This reactor is equipped with a few or more rotary bladed shafts to agitate a mixture in a fixed ratio of pulverized lignite and nitric acid. The feed mixture introduced into the reactor from one end undergoes the reaction and comes out of the other end of the equipment. Nitro compounds produced from the reaction may be subjected to oxidation and recycled for re-use. The reactor under consideration is made of stainless steel to prevent oxidation, and it is constructed large enough to anticipate the boiling over or spilling of the liquid mixture. In fact, the reactor used in accordance with the present invention is believed to be the first of its kind ever known for use in the manufacture of nitro humic acid. In other words I nearly all conventional batch-style equipment operations involve widely varied latent periods in the early stage of reaction and sudden occurrence of reaction which follow upon passage of said latent periods with the result that the majority of reaction products are either in a liquid phase or foamy yet slurry state. These difficulties will be successfully eliminated by the use of the kneader-reactor described and schematically illustrated in the accompanying drawings. It may be mentioned here that nitric acid can be rendered reactive, even if it is of low concentration, by applying sufficient heat, whereas it is well to remember that pure nitric acid of sufficient concentration or about 20% at the least is internally generative of heat at normal temperature. Nitric acid of lower concentration varies in its latent period before it starts to react but at higher concentrations its latency grows shorter. At about 27% concentration the reaction of nitric acid occurs almost instantaneously. This fact obviates the necessity of heat application. At the same time, the fact that the velocity of reaction of nitric acid is generally greater the higher the concentration suggests that the overall length of the equipment can be reduced accordingly. On the other hand, if the concentration is too high a concentration of this acid tends to introduce a loss in the yield of the desired nitro humic acid. Nitric acid when used in 50% or higher concentration causes a rapid decrease in the net yield of the product. It follows from the above discussion that the optimum concentration of nitric acid in the instance of the present invention is substantially between 20% as a lower limit and 50% as an upper limit. The various advantages of the present invention in 10 addition to the continuous reaction procedures made possible by the exothermic heat generation and maintenance of nitric acid as above noted are listed as

follows: (a) i'@To exter-ial heat application is xequired. (b) No critically strict reaeio-.i control is needed. 15 (,G) Sho,,:treactiontime. (d) Reactioii prodilcts coitain a reatlively small ar@iou-@it of ,vater. (e) Li,-p3te or I;ke - 'iamic siibstance as startina, -nate-,ial@s may be used rather coarse. 20 (fl Lowpo-,verferagitationinthereacLor. (g) Low initial cos+s. Attention is no7,v iv@iited to ' h-. rrietiiod f or cont@' nuously n@utraliz;n,- nitro humic -,cid. Conventional processes I of neutrali7 tion eilrploy the reaction -ander llo,- Lilcl- -a 25 pha,-. co@idt,'@ois. To achieve conti.-luous o:@,cration on slch -,) rocesses tremendolis cos,'- is enta-.led for equi-ament and L@cilities. i.,l view of this, ,he pfesent invcnlors conduc@,P-d ext----si7,ic researcia a--qd tests &,/er a period of tr@le ;n an ef-,ort tG @lird and @iscertaii-. the- possibility of a I-qjid- 30 rliase as @,voll@ as a soh-d-pliase reaction for neutralization @f the ocids. For ne,.itralization of nitro hui-.l;c acid in accordarace -vwith the pres--nt -invei- tioTi, rf,@a.-ilesia-cont,,,.iniig @materials i-ene atediieraina@oove, ,,,@hich i-n-.lude magnesite, ma-.nesia, 35 cialomite, s--rpent;ne, silic;c acid magnesi-u-Ln, magr@esium hyOrox,'.-Ile a-,id 'Lbp, 'tike, are useci to -pro--i@jce ria-nesij,,--n sa,ts n -t co@-iti@-iious mo,,,:c c,'L T@il@i.-ig serpen- tiii@,- as an exarii.D!-- , its i-.ois',uirc corl-tent l,emparatu.,e -rate of react;o@i Fr@d wlici these f,,ic- 40 tors are oroperly predetern-iin--d suffici,-nt reaction can take place vtith good The a@noilpt o', ma@nesium- containing material to bc ii-sed may vary wiva th',-- conditions iTi which intro hurnic acid is produced, bIt it is believed that MgO can theoretically react .n about 6 to 7.5 % i5 with nitro humic acid. Exp,-riments indicate tnat in order to retain more than 80% of ritro hiriic acid in the product according to the ires--r@t inver'-@tion, it is rec--ssary to ma-intainthe said prodi,-cl@ at 6C;' C. or al,)ove in the pr,-senr-e of 30% or r-.clr@-I 0l 5o vater for 30 or at 40' C. in th-- preseice ffL 40% o@@- :nore o@t) 7later ,or o'O rpinut--s. Tl,.ese recluirer@ients r-qay be met ivhen the -eae;on -orodur-t from t'--e c- ,n@inuously oi3--rati-iig reactor is - immediately adniixed ivith a rc.-a.-nesium-contairii- mi ater-lal, without having to 511- 3 iply u.,poti exteral heatin,@ sources. Unlike the conve@i- tional batchi oper-@itions i--iriploying neutraliz-,ition after the prorl4 acL is f;!,--red @ind washod, +he Prod,,.ct obta'ied by the prese-@it invention is s-abjected as a whole to n,-utral- @zz,.t ioii -,Yvithoat f@lt--rin.- nitro hiiniic acid fro-in the waste 6- 9 liqil-or. Conseqtiently, ther-. may be retained some low-Pr Thesp @ o,@.d- , matters and ritric- acid in the ciid prod-act fore;g a cor@tents, how-ver, La-,ic been ageertain-ld to be free from adversely aff-@-cting the plants and vegetables under culture, and, in fact, sorde lower organic ac;ds helps 65 . + . : main,a iniig th-. sail to b,- granular and aerati-ve and can b-- adva,2.,agp..ou,,s'@@Y retai-@i;-d i-ii the end I)rodu,-+. of the iii- Venti o-Ti. Th@, i-rosrz@rit havi@i.- been describprd as 'to i+s 70 typ:.Cal processes for producin-, a solid conditioning iinpi-oving co@npound, @ivill n-,w be descri@bed in coilnection with an apparatus er-nljloyefl for th-. said processes. The d@e@cril.-i,ion follovis witli reference to the accompan . ying dre@,wir..as, in Nvwhich: 75 FIG@ I is a Ion-.-tud-inal cro--S-Sect;opal side view of the

Full	Title	Citation	Front	Review	Classification	Date	Reference	Claims	RWC	Draw De
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9. Document ID: US 3190789 A

L2: Entry 9 of 15

File: USOC

Jun 22, 1965

DOCUMENT-IDENTIFIER: US 3190789 A

TITLE: Calcium silicate-filled paper

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The term "acidic material" as herein used includes not only acids but also acid salts, i.e., those having a hydrogen atom replaceable by a metal, whether they are acidic or mildly alkaline in aqueous solution, and normal salts having an acidic reaction. Typical of the acids usable are sulfuric, sulfurous, phosphoric, phosphorous, tartaric, citric, and oxalic acids. Acid salts which react to form insoluble calcium salts include sodium bisulfate, sodium bisulfite, monosodium phosphite, and sodium bicarbonate. A salt such as sodium bicarbonate is less alkaline than calcium silicate, and reacts therewith, reducing the pH of aqueous suspensions of calcium silicate below that which would result with calcium silicate alone. Normal salts which hydrolyze in water to form acidic solutions and react with calcium silicate include aluminum sulfate, ammonium sulfate and aluminum phosphate. In general, a non-oxidizing acid or acid reacting salt whose corresponding calcium salt is insoluble may be used as the acidic material in the present invention, all of the aforementioned substances react with calcium silicate to form a complex precipitate containing silica and more or less of the calcium salt of the acidic material. Whether or not there is any chemical combination between silica and the calcium salt is undetermined. The amount of acidic material such as aluminum sulfate which will establish the aqueous pulp slurries containing calcium silicate pigment at a desired pH varies depending, among other things, upon the nature of the calcium silicate. For example, more aluminum sulfate per pound of calcium silicate pigment is employed with a calcium silicate having a mole ratio of SiO_2 to CaO of 1:1 than with a calcium silicate having a SiO_2 to CaO mole ratio of 3:1. Also, those calcium silicates having low bound water contents, or even essentially no bound water, require less aluminum sulfate in establishing the pulp slurry at desired pH than those with higher bound water contents. If desirable (for the purpose of reducing the aluminum sulfate requirements) as may be the case with otherwise excellent calcium silicates having excessive bound water contents, bound water may be removed from the pigment by heating at temperatures above 100°C . but below about 800°C . The quantity of calcium silicate added to the slurry is enough to provide about 0.5 to about 20 percent of SiO_2 based on the weight of fiber in the pulp. Usually the amount is greater than the stoichiometric quantity for complete neutralization of the acidic material present. When the stoichiometric quantity of silicate is used, all of the CaO therein is neutralized by the acidic material, forming silica and the calcium salt of the acidic material. As has been indicated, the acidic material should be one which forms an insoluble calcium salt so that the precipitate which forms is either a composite of silica and an insoluble calcium salt or some chemical combination of the two. The acidic material is conveniently added to the pulp slurry prior to the addition of calcium silicate. This is not essential, however; the acidic material may be added concurrently with the calcium silicate if desired. Any order of addition of silicate and acid may be followed so long as the pH of the pulp slurry is kept within the proper range at all times. The reactions of calcium silicate with acidic materials are typified by the reaction with aluminum sulfate, in which one mole of aluminum sulfate is reacted with at least three moles of calcium silicate CaO (SiO_2) where x is not less than 2 nor greater than 4 to form a precipitate whose composition may be represented by the formula: $b\text{CaO} \cdot a\text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot c\text{SO}_3$ where a is at least 3, b is equal to or less than 2, and c is equal to or less than a and generally less than b . Small amounts of CaO and SO_3 are dissolved, so that b is at least 3, 190,789 4 are invariably less than a . The maximum value of a is such that the pH of the slurry does not exceed 9.2. Pigment loadings of less than one percent up to 30 percent by weight or even higher have been found to be quite effective for producing paper of high brightness, opacity, and smoothness. Bursting and tear strength are satisfactory in paper sheets prepared according to the present invention, and in some cases tear strength even exceeds that of an unpigmented sheet. 10 The chemical pulps and mechanically ground fibers of low resinous content, i.e., northern pine, spruce, hemlock, are amenable to treatment in acid medium. In a typical procedure for precipitating the pigment of this invention in situ in such fibers, a substance possessing appreciable acidity, as for example, sulfuric acid or aluminum sulfate, is added to a beaten pulp slurry in

sufficient quantity to establish a pH in the range of about 4 to 5.5. Thereafter, calcium silicate is added, reacting with the acid to form a precipitate in situ on the surfaces of the fibers. The amount of calcium silicate is sufficient to react with all of the acid present but is generally less than twice that amount. As calcium silicate is added, the pH of the slurry rises. The amount of calcium silicate added is such that the final pH does not exceed 9.2. Paper produced by this method is suitable for printing, for example, as top liner for box-board cartons. Slight modification of this method to include a precipitated size may be made when writing paper is desired. In the production of writing papers, it is necessary to use 30 size the sheet. A convenient way to produce a sized sheet for writing is to add rosin size (sodium resinate) to the pulp prior to the addition of acid, either before or after the pulp is beaten. A size precipitant, preferably aluminum sulfate, is added either prior to or concurrently with the addition of acid. Other size precipitants, as for example, titanate sulfate, may be used in place of aluminum sulfate. The size is precipitated as a resinate of the heavy metal (usually aluminum). To acidify the pulp slurry, a further quantity of aluminum sulfate, or other acidic material, is added, after which calcium silicate is added. Pulp may be bleached in acid medium, particularly with sulfurous acid or zinc hydrosulfite, prior to pigmentation according to the present invention; In such a process the residual acid in the bleached pulp is not washed out but is allowed to remain. This acid reacts with calcium silicate which is subsequently added, forming a precipitate which includes calcium silicate, an exceptional ly white substance, on the fiber surfaces. Paper can be prepared by addition of calcium silicate to a naturally alkaline pulp slurry in which alkalinity is imparted by an alkaline reacting acid salt such as sodium bicarbonate or disodium phosphate. These salts behave as buffers, so that substantial volumes of calcium silicate can be added to the pulp slurry without raising the pH to an undesirably high level. While any pulp, either chemical or mechanically ground, can be loaded with calcium silicate in an alkaline medium, this method is particularly adaptable to the pigmentation of mechanically ground fibers of highly resinous woods such as southern pine. In a typical operation in alkaline medium, an aqueous slurry of kraft process and mechanically ground southern pine fibers is prepared or beaten, and an acid salt (that is, one having a hydrogen atom replaceable by a metal) which is mildly alkaline is added to the slurry. This addition is omitted in the event an appreciable quantity of such compound is present in the water in which the pulp is slurried. Calcium silicate is then added. Loadings of about 3 to 30 percent by weight of calcium silicate based on the weight of dry pulp have been found to be good for production of a paper sheet having a smooth surface in addition to high brightness and opacity. In no event is the amount of calcium silicate so great as to cause the pH of the slurry

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were otherwise prepared in the same manner as the test sheets. The following results were obtained: Table Y Filled Sheets Control Sheets Uncoated Coated Uncoated Coated J3riglitiaoss (G.E.): Felt side ----- 64.7 69.3 60.6 67.3 Wire side ----- 64.5 68.4 61.4 67.5 Opacity (Bauscht Lomb) --- 80.8 91.6 75.8 89.8 Smoothness (Sheffield): Felt side ----- 227 -- ----- 172 Wire side ----- 224 165 Gloss: Felt side ----- 42. 4 ----- 37.0 Wire side ----- 40. 6 ----- 36.5 Tensile strength: Machine direction ----- 4.8 7.22 6.0 7.61 Cross direction ----- 3.4 4.11 4.2 5.55 Bursting strength (initially) -- 10.7 13.61 12.7 15.65 Tear strength of oven dried sheet (about 1% moisture by weight): Machine direction ----- 21.7 20.3 20.4 19.5 Cross direction ----- 26.9 23.8 24.9 23.0 Tear strength of air dried sheet (about 5% moisture by weight): Machine direction ----- 39.7 28.9 38.9 29.5 Cross direction ----- 43.0 33.1 44.5 30.3 M.I.T. fold test: Machine direction ----- 221 274 395 529 Cross direction ----- 105 305 461 927 EXAMPLE VI A pulp slurry containing about 3 percent pulp by weight was prepared by adding kraft process southern pine pulp and mechanically ground northern spruce pulp to a tank equipped with an agitator at a rate of 300 pounds of pulp (dry basis) per hour.

About 50 percent of the total weight of pulp was kraft pulp. The slurry was pumped to a stock chest and thence to a mixing chest, where it was diluted to a consistency of about one per cent pulp by weight and mixed with an aqueous slurry of calcium silicate. The slurry of calcium silicate which was added to the beater was prepared by adding dry finely divided amorphous calcium silicate to water in a mixing vessel equipped with an agitator to form a slurry containing 0.5 pound of calcium silicate per gallon of water. The calcium silicate had an average ultimate particle size of about 0.3 micron, and contained approximately 18 percent by weight CaO, 66 percent SiO₂, 4 percent free water and 12 percent bound water by weight. This corresponds to a ratio of 3.3 moles of SiO₂ per mole of CaO. The calcium silicate suspension was fed to the mixing chest at different rates, which were increased as the run progressed. At the outset the suspension was pumped to the mixing chest at the rate of 48 gallons per hour, and was thereafter raised to 90 gallons per hour, and then to 180 gallons per hour. These amounts corresponded to 24, 45, and 90 pounds of calcium silicate per hour respectively, or 8, 15 and 30 percent by weight of calcium silicate based on the dry weight of fibers. After mixing of the slurries of pulp and calcium silicate, the slurry containing both ingredients was pumped to a head box, from which it flowed on to the wire of a Fourdrinier machine 55 inches in width. Approximately 5 minutes on the average elapsed from the time the calcium silicate was mixed with the pulp slurry until paper was formed. The water drawn through the wire was continuously recirculated. Some pigment was washed out in the water drawn through the wire, so that the ratio of ash to wood fibers in the finished paper was slightly less than the ratio of pigment to pulp in the slurry coming on to the Fourdrinier machine. The paper web moved at the rate of 300 feet per minute, through press rolls and driers. Samples of the dried web were tested for brightness and opacity with a Hunter reflectometer. Opacity as reported is the ratio of brightness of a single sheet with a black backing to the brightness of the same sheet with a white backing. Results were as follows:

Sample	Percent Ash	Brightness	Opacity
65.2	10.21	0.65.6	---
3	0.66.2	4	---
0.62.2	5	0.62.6	6
7.4	69.6 76.9 7	9.9 70.6 77.4	8
10.2	71.0 76.9 9	14.0 72.0	

80.6 Appreciable improvement in brightness was achieved with the brightness improving as the percentage of calcium silicate is increased. 2) Samples of paper filled with calcium silicate were found to receive printing ink satisfactorily, the characters printed on the sheet being sharp and black. Unfilled paper produced from the pulp described in this example was found to be unsatisfactory for printing, because the surface had numerous small spots which did not receive ink. As the foregoing examples show, considerable improvements in the smoothness and gloss of paper containing kraft process southern pine pulp are effected by incorporation of an alkaline earth metal silicate. Most effective in this regard is a finely divided calcium silicate containing no organic matter such as cellulose and starch. The pigments of the present invention improve the brightness and opacity of papers prepared from a mixture of kraft and ground wood fibers, and reduce tensile and bursting strengths only slightly. Some improvement in the smoothness, gloss, and brightness of paper sheets prepared in whole or in part from woods other than southern pine is effected by incorporation of an alkaline earth metal silicate in alkaline solution according to the present invention. Examples V and VI show the beneficial effect of loading a paper prepared from kraft process southern pine and northern spruce ground wood pulp, for example. Northern woods are of higher quality than southern pine for printing paper, and inclusion of an alkaline earth metal silicate filler in pulps of northern woods does not improve paper made therefrom as much as it improves paper made from southern pine. Furthermore, northern woods have a lower resin content than southern pine, so that processing in a basic medium is not necessary. In fact, it is frequently preferred to process northern woods in an acid medium, e.g., at a pH below 7 but no less than about pH 4, rather than in a basic medium as is necessary when using southern pine or other sources of pulp having comparably high resin contents.

Thus, a typical pH for the slurry of a northern wood pulp (or low resin content wood pulp) and pi,-Ment fed to the wire of a paper making machine is between 4.5 and 6.5. 60 The above description has been directed primarily to embodiments wherein the calcium silicate is prepared by continuous mixing of flowing streams of sodium silicate and calcium chloride and the calcium silicate has the composition $\text{CaO}(\text{SiO}_2)_x$, where x is about 2 to 4. 65 It is obtained using such calcium silicates which have been so made. However, calcium silicate of somewhat lower surface area produced by a batch process in which the sodium silicate is added to a pool of calcium chloride solution or vice versa also may be used. Moreover, other water insoluble calcium silicates including mixed silicates of calcium and other metals may be used, particularly when the silicates have an average ultimate particle size below about one micron, preferably below 0.1 micron. Such silicates include calcium aluminum silicates, calcium sodium aluminum silicates, calcium

Full	Title	Citation	Front	Review	Classification	Date	Reference	Claims	RMWC	Draw De
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10. Document ID: US 3079211 A

L2: Entry 10 of 15

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Feb 26, 1963

DOCUMENT-IDENTIFIER: US 3079211 A
TITLE: Treatment of tanned leathers

OCR Scanned Text (1):
United States Patent Office 31079,211 3,079,211 TREATMENT OF TANNED LEATHERS
Ilexime Paquet, Route de Nice, Cuers (Var), France No Drawing. Filed Sept. 28, 1959, Ser. No. 842,605 Claims priority, application France Mar. 23, 1956 5 19
Claims. (Cl. 8-94.21) The present invention relates to the treatment of leathers tanned with zirconium based tanning baths, with a view to controlling their water absorbing properties as well as their permeability to air. This is a continuation-in-part of my co-pending application Serial No. 641,458, filed February 21, 1957, now abandoned. It has been found and verified since a number of years 15 that tanning with zirconium, when properly conducted can produce leathers which are very resistant to wear and friction. However, such leathers have the serious drawback of absorbing too high quantities of water, which restricted their use. Various attempts have been made in different directions to decrease the said water absorption but such attempts have led either to a destruction of the favorable properties resulting from zirconium tanning, or to make the treated leathers impervious to air, and finally no satisfactory solution has been found. 25
The object of my invention is to provide zirconium tanned leathers the water absorption qualities of which are conveniently controlled without impairing their permeability to air, or their resistance to wear. I have found that if fibers of zirconium tanned leather 30 are put in contact with higher fatty amines in proper conditions, the said amines form with the acid reacting zirconium compounds which are fixed on said fibers, highly water repellent compounds which are also solidly fixed on the fibers and which durably impart their water repellancy to the treated leather. It would seem that an inversion of electric charges occurs, although this is a mere supposition. The fatty amines which are operative in my invention are the long chain primary amines derived from fatty acids. of the general formula R.NH_2 in which R is an unsubstituted aliphatic chain having from 8 to 22 carbon atoms. Such amines may be considered as deriving from ammonia through replacement of one hydrogen atom by a fatty chain without any other substitution. 45 Appropriate amines are caprylamine (C8), caprylamine (C10), laurylamine (C12), myristylamine (C14) palmytylamine (C16), stearylamine (C18),

oleylamine (C₁₈), arachidylamine (C₂₀), behenylamine (C₂₂) and the like, the above list not being limitative. The average 50 molecule weights of said amines range from about 130 to about 320. Although all the above amines give favorable results the best results are obtained with oleylamine or palmitylamine, and natural or artificial mixtures of various amines having 16 or 18 carbon atoms may be used satisfactorily in my invention. For example, I obtain good results with the mixture of oleylamine stearylamine and palmitylamine with a dominant proportion of oleylamine, as obtained when treating commercial fatty acids. Generally speaking, I prefer using amines derived from unsaturated fatty acids such as oleic or linoleic acids, rather than amines deriving from saturated acids. However, mixtures containing both types of amines are suitable, and in fact often necessary when special detailed effects are desired. By commercial higher aliphatic or fatty amines, I mean herein products of the modern chemical industry obtained by treating with ammonia, fatty acids having C₈ to C₂₂ chains, whether alone or in natural mixtures, in liquid or gaseous phase, at a given temperature and in Patent of Feb. 26, 1963 suitable conditions. Intermediary products are thus obtained, to wit nitriles, which are thereafter hydrogenated to the commercial fatty amines used in my invention. The intermediary nitriles give no results in the method according to my invention. The above defined amines are neither pure products, nor products which can be defined other than by their method of manufacture but the primary amines of the fatty acids employed are largely dominant, which is sufficient for my process. It is neither recommended nor necessary to use more complicated amines than those above-mentioned, e.g. amines comprising multiple conjugated linkages, no particular or favorable effects being obtained therewith. Although the above defined amines alone are adapted to give the desired results, I have found that the diamines of the same above mentioned fatty acids, which diamines are obtained by similar methods and often in more or less great quantities at the same time as the primary amines also give satisfactory results and may be used in conjunction with said primary amines. Said diamines may be represented by the general formula: R-NH-CH₂-CH₂-NH₂ in which R has the same meaning as above. The said diamines thus comprise both a primary amine group and a secondary amine group. Like the above mentioned primary fatty amines, they are strong bases and they have similar general properties with however a moderate pronounced polarity and a stronger cationic character. It would appear that most of the commercial fatty amines, due to their method of preparation, contain more or less important quantities of such diamines. All the above mentioned amines and diamines are solid or liquid according to the degree of saturation of the fatty chain, and to their molecular weight. They are insoluble in water and soluble in mineral oils, in hydrocarbons, more particularly when added with alcohol, in ethyl, methyl, isopropyl alcohols and the like, and in chlorinated solvents such as trichlorethylene, perchlorethylene or carbon tetrachloride. All said amines and diamines react with organic or mineral acids to give salts the properties of which largely depend on the acid which is used. Thus, most of the monoacids such as hydrochloric, acetic, formic, lactic acids and the like give water soluble salts. The chlorides are soluble in water and soluble in oils whereas the acetates and formates are soluble both in water and in hydrocarbons, as well as in chlorinated solvents. Organic or mineral diacids of higher polyacids generally give salts which are insoluble in water and variously soluble in various solvents. According to my invention, leathers must be treated by amines of the above mentioned type, which have been wholly or partly neutralized by an acid or acids, because of their strongly basic properties, the said neutralized amines being dissolved either in water or in organic solvents depending on the neutralizing acid and the results which it is desired to achieve. I have found that the solutions in organic solvents should be preferred for the treatment of thick leathers, whereas aqueous solutions may be used for the treatment of thin or highly porous leathers. More particularly for the treatment of thick or "heavy" zirconium tanned leathers, the amines or mixtures of amines and diamines are dissolved in an organic solvent or a mixture of such solvents, then neutralized by adding to said solution one or more convenient acids. Preferred amines are oleylamine, linoleylamine, palmitylamine and stearylamine or mixtures

thereof and the solvent should preferably be trichloroethylene or a hydrocarbon.

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3 I have found that for neutralizing the amine or amines, tartaric acid should be used in a quantity equal to at least half the total quantity of acid which is necessary for complete neutralization. The said acid should be preferably added in powdered form, while stirring, to the amine solution maintained between 60 and 70° C. The reaction is exothermic and care should be taken to avoid a temperature rise above 80° C, which could result in an unfavorable transformation of amines into amides. I have also found that part of the basicity of the amines readily and quietly be neutralized by means of very weak acids such as phenolic acid (phenol) or acetic acid (acetic). The presence of such weak acids is useful even when the amines are completely neutralized by means of tartaric acid. Tartaric acid may be in part replaced by citric, sulfuric, sulfurous or phosphoric acid. Cresol may be used instead of phenol and any other resin having an acid reaction instead of abietic acid. I have further more found that the addition of a small quantity of boric acid to the tartaric acid substantially improves the results obtained. It seems that borotartaric acid is formed, which acts favorably as a catalyst of the various subsequent reactions in the presence of the fibers of leather tanned with zirconium. Since the amines employed have a totally basic character which it is easy to estimate quantitatively, these amines should be neutralized by: The tartaric acid (plus boric acid when so required) should be comprised between 50% and 100% of the quantities necessary for the total neutralization of the basicity of the amines; The boric acid should amount to between 0 and 20% of the quantity of tartaric acid; the phenol (CGHBOH) or cresol should comprise between 10% and 50% of the total quantity of amines existing in the solution, this total being calculated in pure amines (according to their quantitative basicity); The acetic acid should preferably comprise between 20% and 90% of the same total weight of the amines. These solutions in trichloroethylene are stable at temperatures which do not exceed 75° C. They are characterized by a high fluidity, a high degree of penetration into the leather or other porous materials, and by their special properties of becoming fixed on products having an acid reaction. For the treatment of heavy leathers tanned with zirconium, these solutions should be employed with a content of amines (calculated in pure amines) comprised between 3% and 15% of their weight. The leathers tanned with zirconium or with mixed mineral tannings, brought to a pH value between 3.5 and 5.0, carefully washed and then dried or almost dried, are soaked for 10 to 40 minutes in the solution described above, maintained between 15° and 50° C., depending on the case, and then dried in air at a temperature not exceeding 40° C. The results are improved by operating in a closed tank in which a certain depression is maintained, for example 30 cm. of mercury. The solvent may be recuperated by drying in an appropriate apparatus with or without vacuum. The leathers thus treated and dried are already strongly water-repellent and can be used commercially in that state in certain cases. They have however generally been subjected to excessive dehydration, which modifies their properties and their appearance. It has been found that it is useful to subject them to a controlled hydrolysis, during which they fix a small quantity of water and recover an average general humidity, which can be estimated by the usual method, comprised as required between 12% and 18%. This hydrolysis is effected by soaking the leathers as treated above and dried for one hour or more, in a bath of water maintained between 40° and 50° C. During the course of this operation, the appearance and colour of the leathers change completely and their water-repellent characteristics are considerably increased after they have been dried. To this bath of water, there may be added when so required, small quantities of particular reagents (for example various organic acids) so as to modify certain details relative to qualities and appearance. The application of the invention is illustrated in the examples given in the following text. These examples are understood to be illustrative only, and the invention is in no way limited by the indications given therein.

Example I 15 Heavy butts of cow leather are strongly tanned with zirconium following a standard method with a very acid pH value (about 1.5) and with about 6.5% of zirconium oxide calculated on the weight of leather butts in strips. 20 The completely tanned skins are rendered basic in a tanning bath up to a pH value of about 3.0 and are then neutralized in a fresh bath to a pH value of 4.0 to 4.5 and carefully washed. If so desired, they are then rapidly surface-dyed by 25 soaking for about one hour in a light bath of a vegetable tannin extract (for example elhestnut) so as to obtain a pleasing appearance. The leathers are then allowed to drain, dried and then rolled. They give by analysis about 15% humidity. 30 At this stage, the leathers show a water absorption of 65% to 70% with the Kubelka apparatus in one hour, and have an excellent resistance to wear. The leathers are then treated as below so as to render them water-repellent and to give them special qualities. 35 For this purpose, an impregnating solution A is made: In: 1200 kg. of trichlor-ethylene there is dissolved while heating to 60° C.: 100 -kg. of commercial oleyl-amine containing 92 kg. of primary fatty amines composed of palmitylamine 7 kg., stearyl-amine 4 kg. oleyl-amine 81 40 kg., the average molecular weight of these amines being 268. The estimation of the basicity showed that 29.6 kg. of pure, tartaric acid would be necessary to obtain complete neutralization. To this solution, kept at 60° C., there is slowly added: 45 25 llg. of tartaric acid and 2.5 kg. of boric acid, both these acids being in the form of powder. After complete reaction, which requires about 12 hours, 28 kg. of phenol are added, followed by 47.5 kg. of colophane. 50 After leaving to rest for 3 days, this solution A is ready for use. There is thus available about 140-0 kg. of a solution containing about 6.6% of oleyl-amine, 2% of phenol and 3.4% of colophane. 100 kg. of the zirconium leathers referred to above 55 are soaked for 30 minutes in the impregnating solution A, maintained at 45° C. The leathers are removed from the bath; after draining they weigh about 140 kg. (before drying). They have fixed about 2.7 kg. of fatty amines, or 2.7%. 60 The leathers are completely dried in air between 20° and 35° C., after which they give the following water absorption in the Kubelka apparatus: 9 to 10% in 1 hour 16 to 18% in 3 hours 65 34 to 38 % in 24- hours The impregnated and normally-dried leathers give on analysis a humidity content of 8 to 10%. The glue on these leathers with neoprene glues is possible, but necessitates very extensive carding of the 70 surfaces. Example 2 The leathers obtained by the treatment of Example I are again treated to give a hydrolysis. To this end, they 75 are soaked for one and a half hours in a bath of water

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5 held at 45° C., after which they are dried in air between 20° and 35° C. After drying, their colour is much lighter and more uniform and their appearance is definitely more pleasing. With the Kubelka apparatus, they give the following degree of water absorption: 5 to 7% in 1 hour 8 to 9 % in 3 hours 26 to 29% in 24 hours When normally dried, these leathers give 14 to 16% humidity on analysis: they can readily be glued. Example 3 100 kg. of the same zirconium leathers are impregnated with the same solution A, but this operation is carried out in a suitable tank, in which is maintained a temperature of 45° C., and a depression of about 30 cm of mercury. The period of impregnation is 25 minutes, after which the solution is evacuated and the leathers are left in the tank. The solvent is then evaporated in the tank itself, in which is maintained a depression of 10 to 20 cm. of mercury. After 40 minutes in a suitable apparatus, about 90% of the solvent used for the impregnation is recovered in this way. The leathers are removed from the tank and completely dried in air at about 30° C. After leaving to rest in this state, a hydrolysis treatment is made, as in Example 2 above, but with water at 45° C. to which there has been added 1 part in 10,000 of its weight of ethylene-diamine tetracetic acid. The leathers thus obtained and dried are of very light colour and pleasant appearance. It is found by analysis that they have fixed 3.5% of fatty amines and that they have an average humidity of 14 to 16 %. With the Kubelka apparatus, these leathers give greatly improved water-absorption characteristics as follows: 3 to 5 % in 1 hour 7 to 8% in 3 hours to 24% in 24 hours These leathers can be glued perfectly and without any difficulty. To, ether

with a very low water-absorption characteristic, they have an excellent and substantially increased resistance to wear together with mechanical, physical and chemical properties which are both new and very favorable, in particular exceptional resistance to pulling off, tearing and abrasion. Example 4 The same process is followed as for Example 3 but the impregnating solution employed is obtained with the following mixture: Commercial oleyl-amine: 50% Commercial stearyl-diamine: 50% For the neutralization of 100 kg. of this mixture, the quantity of tartaric acid is brought up to 29 kg., the other constituents remaining unchanged. The impregnating operation and the hydrolysis process are the same as for Example 3. The results obtained are also comparable with those obtained in Example 3, namely: Similar water absorption characteristics; The leathers are darker with a more greasy appearance; The leathers are softer and more flexible; The resistance to tearing is exceptionally high. Example 5 The same process is followed as in Example 3, but the impregnating solution is obtained by using the mixture of fatty acids from ordinary tallow. This mixture contains: About 30% of palmityl-amine About 40% of oleyl-amine About 30% of stearyl-amine The neutralization of the solution is obtained as in Example 3, the other constituents remaining unchanged. The operation of impregnation and hydrolysis are effected in the same way as in Example 3. The results obtained are closely similar to those described in Example 3, but the leathers are stiffer, their appearance is less pleasing, and the favorable effects of hydrolysis are reduced. Example 6 The same process is employed as for Example 3, but the impregnating solution is obtained by utilizing the mixture of fatty amines resulting from the treatment of the natural mixture of fatty acids in copra oils. This mixture gives on analysis the following approximate composition: Percent Capryl-amine (C8) ----- 8 25 Capryl-amine (C10) ----- 47 ----- 9 Lauryl-amine (C12) ----- 47 Myristyl-amine (C14) ----- 18 Palmityl-amine (C16) ----- 8 Stearyl-amine (C18) ----- 5 30 Oleyl-amine (C18) ----- 5 The average molecular weight of these amines is 196. The neutralization of the solution is carried out as in Example 3, with the exception that 32 kg. of tartaric acid are added to 100 kg. of the above amines in solution; the other constituents remain unchanged. The operations of impregnation and hydrolysis are the same as in Example 3. The leathers obtained give the following water-absorption characteristics with the Kulbelka apparatus: 12 to 15% in 1 hour 18 to 20% in 3 hours 36 to 42% in 24 hours The water-repellent effects are definitely less than in the case of Example 3, but they will often be adequate. The leathers are flexible, light in colour and of very pleasant appearance. Example 7 The same process is followed as in Example 3, but the impregnating solution is obtained by employing the mixture of fatty amines resulting from the treatment of the fatty acids of hydrogenated tallow, which are thus saturated fatty acids. This mixture of amines has the following approximate composition: Percent Palmityl-amine ----- 30 Stearyl-amine ----- 68 60 Oleyl-amine ----- 2 The average molecular weight of these amines is 265. The neutralization of the solution is carried out as in Example 3, employing the same acids and the same other constituents. The operations of impregnation and hydrolysis are also the same as those described in Example 3 and give similar results in respect of water absorption, but the leathers are firmer, darker in colour and have a less pleasing appearance. The favorable effects of hydrolysis are reduced and the leathers are more difficult to glue with standard neoprene glues. Example 8 The same process is followed as in Example 3, but the impregnating solution is obtained with a mixture of

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7, fatty amines derived from commercial fatty acids with 20 to 22 atoms of carbon. This mixture has the following approximate composition: Percent Arachidyl-amine (C20) ----- 56 Behenyl-amine (C22) ----- 35 Stearyl-amine (C18) ----- 9 The average

molecular weight of these amines is about 310. The neutralization of the solution is carried out as in Example 3, but only 20 kg. of tartaric acid are employed for 100 kg. of the above anilines; the other constituents remain unchanged. The operations of impregnation and hydrolysis are carried out in the same way as in Example 3. The leathers obtained are very firm, of dark appearance and their surface feels greasy to the touch. They are difficult to glue, but the water absorption properties are excellent. Leathers of this kind can have valuable features for certain particular cases. The examples given above can be summarized by stating that the use in the process of the present invention of oleyl amine and mixtures of oleyl-amine and linoleylamine (unsaturated fatty chains) give the most favorable results in the majority of the usual cases, but the other amines may produce leathers which have certain characteristics specially suitable for particular cases. Example 9.—Replacement of a Part of the Tartaric Acid, in the Above Examples, by Another Polyvalent Acid The same procedure is followed as in Example 3 above. The impregnation solution is obtained with commercial oleyl-amine which gives by analysis the following composition: Percent Oleyl-amine ----- 85 P, almityl-amine ----- 10 ----- Stearyl-amine ----- 5 The average molecular weight of the above amines is about 270. The neutralization of the solution containing 100 kg. of these amines is carried out as in Example 3, except in that the following are added: Kg. Tartaric acid ----- 16 Boric acid ----- 2 Citric acid ----- 10 The above acids are in powder form. The other constituents remain unchanged. The operations of impregnation and hydrolysis are also the same as in Example 3. The leathers obtained have similar characteristics to those of the leathers of Example 3, with the following observations: The water absorption percentages are higher; The penetration of the amine compounds into the leather is less uniform, due to the greater viscosity of the impregnating solution; The leathers have an excellent appearance. From a large number of tests made by substituting another acid for part of the tartaric acid, the following conclusions have been reached: The replacement of part of the tartaric acid by sulphuric acid, sulphurous acid, phosphoric acid and other polyvalent acids, taking account of their valency and their molecular weight, results in solutions the viscosity of which increases with the quantity of these acids employed, while the penetration into the leathers diminishes rapidly. On the other hand, the water-repellent effects are favorable. The replacement of part of the tartaric acid by a monovalent acid—hydrochloric acid, acetic acid, formic acid, lactic acid, etc., rapidly results in excessive water absorption as measured with the Kugel apparatus. This effect can be employed to regulate the water absorptivity to any value desired, according to the case. Example 10.—Influence of the Solvent Used The same procedure is followed as in the case of Example 3, the same amines, same operations of neutralization, and the same addition of the other constituents, but the 1200 kg. of trichlor-ethylene (impr)regnating solution A) are replaced by 750 kg. of ordinary benzene (density 0.9, boiling point 81.1 C.). The operation of impregnation and hydrolysis are carried out as in Example 3. The results obtained are in all respects very similar to those obtained with trichlor-ethylene employed as the solvent in Example 3, the conditions of recovery of the solvent aid of drying being of course appropriate to the solvent and the necessary precautions being taken in view of its inflammability. It has been found that the results obtained with these 20 leathers, within the framework of the present invention, vary very little with the solvents employed, provided that the latter are taken from the family of chlorinated solvents (tetrachlor-ethylene, perchlor-ethylene, carbon tetrachloride, etc.), or from the family of hydrocarbon solvents (benzene, toluene, naphtha solvents, etc.). The choice of the solvent from the above groups should be made by taking account of their solvent qualities for the amine compounds, of their physical properties (density, boiling point, speed of evaporation, etc.), of their facility of use and of recovery within the scope of their commercial utilization. It has been found that alcohols can be employed as solvents, especially when another solvent is added, since generally speaking, the alcohols rapidly reduce the water content, 5

repellent properties of the leathers treated, resulting, in water absorption percentages, as given by the Kubelka apparatus, which rapidly become excessive with increasing proportions of alcohol used as a solvent (ethyl alcohol, methyl alcohol, isopropyl alcohol, etc.). 40 claim: 1. A method for imparting water repellency to leathers tanned with a zirconium based tannin bath, while maintaining high resistance to wear and high permeability to air, which comprises impregnating said leather with a solution in an organic solvent of compounds selected from the group consisting of a higher aliphatic primary amine of the general formula $R-NH_2$ and compounds selected from the group consisting of an amine of the general formula $R-NH-CH_2-CH_2-NH_2$ in which R is an aliphatic chain comprising 8 to 22 carbon atoms and mixtures of said amines, said amines having been previously combined with tartaric acid in at least one-half the amount required to neutralize said amine, and thereafter hydrolyzing said leather by soaking in water at a temperature between about 25 and 55° C., and drying said hydrolyzed leather in air. 2. A method as claimed in claim 1, in which the amine 60 is commercial oleylamine. 3. A method as claimed in claim 1, in which the soaking solution is a solution of a mixture of amines derived from the fatty acids of copra oils, containing a major proportion of aliphatic chains containing 10, 12 and 14 carbon atoms. 4. A method as claimed in claim 1, in which the soaking solution is a solution of a mixture of primary fatty amines derived from the fatty acids of tallow having chains containing 16 and 19 carbon atoms, of which fatty acids about 40% are constituted by oleic acid. 5. A method as claimed in claim 1, in which is used a mixture of primary fatty amines derived from commercial oleic acid, said amines containing a proportion of at least 85% of oleyl-amine. 6. A method as claimed in claim 1, in which the

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ing solution is a solution of a mixture of primary fatty amines derived from hydrogenated tallow the predominating quantities in said amine mixture being constituted by stearyl-amine and palmityl-amine. 7. A method as claimed in claim 1, in which the soaking solution is a solution of a mixture of primary fatty amines having chains with 20 and 22 atoms of carbon, the preponderant quantities in said amine mixture being constituted by arachidyl-amine and behenyl-amine. 8. A method as claimed in claim 1, in which said impregnating solution comprises quantities of fatty amines comprised between 3% and 18% by weight, calculated in pure amines before neutralization. 9. A method as claimed in claim 1, in which to said impregnated solution are added the following: 10 to 40% of tartaric acid of the weight of the amines and diamines, calculated in pure amines or diamines; from 0 to 40% of phenol or cresol of the weight of the amines and diamines, calculated in pure amines or diamines; from 10 to 90% of colophane of the weight of the amines and diamines, calculated in pure amines or diamines; from 0 to 20% of boric acid, calculated on the weight of tartaric acid used. 10. A method as claimed in claim 1, in which the solvent employed for said soaking solution is a chlorinated solvent. 11. A method as claimed in claim 1, in which the solvent employed for said soaking solution is a hydrocarbon. 12. A method as claimed in claim 1, in which the solvent employed for said soaking solution contains at least one alcohol in a proportion not exceeding 50%. 13. A method as claimed in claim 1, in which part of the tartaric acid employed in said soaking solution is replaced by a polyvalent acid selected from the group consisting of citric acid, sulphuric acid, sulphurous acid, phosphoric acid, this substitution not exceeding 40% of the total quantity of acid necessary for the complete neutralization of said amines. 14. A method as claimed in claim 1, in which at least a part of the tartaric acid employed in said impregnating solution is replaced by a monovalent acid selected from the group consisting of hydrochloric acid, acetic acid, formic acid, lactic acid, this substitution not exceeding 25% of the quantity of acid necessary for the complete neutralization of said amines. 15. A method as claimed in claim 1, in which the water employed for the hydrolysis of said leathers is acidified by the addition of a small quantity of an acid. 16. A method as claimed in claim 15, in which said acid is ethylene-diamine tetracetic acid. 17. A method for imparting water repellency to leather tanned with a zirconium based tannin bath, while

maintaining high resistance to wear and high permeability to air, which comprises impregnating said leathers with a solution in an organic solvent of compounds selected from the group consisting of a higher aliphatic primary amine having an aliphatic chain of 8 to 22 carbon atoms and mixtures of said amines and previously combined with tartaric acid in at least one-half the amount required to 15 neutralize said amine, said solution also containing phenol and colophane and evaporating said solvent. 18. A method for imparting water repellency to leathers tanned with a zirconium based tanning bath, while maintaining high resistance to wear and high permeability to air, which comprises impregnating said leathers with a solution in an organic solvent of compounds selected from the group consisting of a higher aliphatic amine of the general formula $R-NH-CH=CH-CH=NH_2$ 25 in which R is an aliphatic chain comprising 8 to 22 carbon atoms and mixtures of said amines, said amine having been previously combined with tartaric acid in at least one-half the amount required to neutralize said amine, said solution also containing phenol and colophane. 19. A method as claimed in claim 18, in which the soaking solution is a solution of a mixture of primary fatty amines and fatty diamines, said amines and diamines being constituted by fatty chains having from 12 to 20 atoms of carbon. References Cited in the file of this patent UNITED STATES PATENTS 40 2,343,920 Maxwell ----- Mar. 14, 1944 2,868,833 Szabo et al - ----- Jan. 13, 1959 FOREIGN PATENTS 452,630 Great Britain ----- Aug. 21, 1936 45 OTHER REFERENCES J.A.L.C.A., March 1959, page 178, vol, LIV, No. 3,

Full	Title	Citation	Front	Review	Classification	Date	Reference	Claims	Notes	Drawings
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11. Document ID: US 3016399 A

L2: Entry 11 of 15

File: USOC

Jan 9, 1962

DOCUMENT-IDENTIFIER: US 3016399 A

TITLE: Cholinphosphoric acid salts and production thereof

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31010,399 3 MY invention further comprises the production of cholinphosphates of metals (such as sodium and potassium) to which correspond a hydroxide showing a definitely alkaline reaction in aqueous medium and a water soluble phosphate, and the production of cholinphosphates of metals (such as cobalt) to which corresponds hydroxide which is not alkaline in aqueous medium, by means of a double decomposition from magnesium cholinphosphate or an alkali earth, e.g. calcium, cholinphosphate and a salt of an acid which yields a water-insoluble magnesium or alkaline earth metal salt. My invention also includes the salts of cholinphosphoric acid having a betain structure which may be produced by the process above described, more particularly the following salts (the formulas thereof being written according to the second form thereof): (a) Magnesium cholinphosphate: $(H_3C)_3N-CH_2-CH_2-O-P-O-Mg \cdot 4H_2O$; (b) Calcium cholinphosphate: $(H_3C)_3N-CH_2-CH_2-O-P-O-Ca \cdot 10H_2O$; (c) Cobalt cholinphosphate: $(H_3C)_3N-CH_2-CH_2-O-P-O-Co \cdot 15H_2O$; (d) Ferrous and ferric cholinphosphates $(H_3C)_3N-CH_2-CH_2-O-P-O-Fe$, $(H_3C)_3N-CH_2-CH_2-O-P-O-Fe$, p 11 (where m and p denote various degrees of hydration); and the aqueous solutions thereof. The above salts particularly the magnesium and cobalt salts and aqueous solutions thereof are valuable for therapeutics, the magnesium salt being useful by reason of its lipotropic activity thereof while the cobalt salt and iron salts are useful for the treatment of specific forms of anemia. They may be employed in

mutual - associa- and also in association with cholinphosphate chlo-, A rides; for example the ferrous salt may be associated with the chloride of calcium choline phosphate. 55, Moreover by adding the calculated amount of sulphuric acid to an aqueous solution of say calcium or barium cholinphosphate and removing the precipitate, substantially pure cholinphosphoric acid having a betain (10 structure may be produced in a more simple manner than proposed heretofore. The magnesium salt of cholinphosphoric acid having a betain structure was found to have a lipotropic - activity and a liver protecting activity superior to those of cholin (5 and methionin. I believe that the activity of that magnesium salt is due chiefly to phosphoryleholin which is more active, than cholin in the metabolism of lipids and is a direct intermediate. in the biosynthesis of lecithin. -

N; cholinphosphate having a betain structure 70, pure magnesium salt is a higher phosphorylcholin content than calcium cholinphosphate chloride. which as far as I am aware is at this time the only compound out of that series employed for therapeutic purposes, the content being 94.4 to 72 percent in the case of calcium cholinphosphate chloride (also reckoned in anhydrous state). On the other hand I consider the magnesium ion to be more favorable than the calcium ion, particularly in various metabolic diseases, more especially in arteriosclerosis. Finally my magnesium salt does not contain chlorine ion known to have an unfavorable action in water retaining phenomena bound with liver diseases (cirrhotic ascites). For those reasons my magnesium salt is useful in hepatology and presumably in the treatment of arteriosclerosis. A pharmaceutical form suitable for oral administration is aromatized granules containing 10 percent by weight of my magnesium salt.

Suitable daily doses for oral administration range from 0.50 to 3 g. For parenteral administration, aqueous solutions prepared in advance are not desirable because my magnesium cholinphosphate is subject to a hydrolysis in aqueous media which is fairly slow at ordinary temperatures but results in the production of a slight precipitate of magnesium phosphate. Consequently I prefer solutions in pharmaceutically acceptable anhydrous organic solvents, particularly triethylene glycol. As the production of a precipitate of magnesium phosphate is slow; it is also possible to deliver my magnesium salt in ampullas or small bottles for dissolution into physiological saline solution at the time of use; the solution may be given a slightly acid pH-value e.g. by means of citric acid or any other pharmaceutically acceptable acid, with a view to compensating for the alkalinity of my magnesium salt and thus to provide a substantially neutral solution for injection. In the parenteral administration of my magnesium salt in the form of solution thereof as aforesaid, daily doses: from 0.50 g. to 4 g., even larger doses, have been administered clinically for the treatment of liver diseases without causing toxic phenomena. The cobalt salt of cholinphosphoric acid having a betain structure, was found to cause a significant increase of the number of red blood corpuscles in young mice in the period of weaning, such action being still greater where the said salt is associated with an iron cholinphosphate, for example with ferrous cholinphosphate chloride of the formula $(\text{HAc})_3\text{ENaClIr-Clr}_2\text{-O-P}\backslash\text{Fe}^{+1}\text{ClO}$ An effective hematopoiesis-stimulating medicine in granular form for oral administration has the following formulation G. Calcium cholinphosphate chloride ----- 7 Ferrous cholinphosphate chloride ----- 1.5 Cobalt cholinphosphate ----- 0.40 Citric acid -----

----- 2 Sugar and perfume to make up ----- 100 The following examples which are not limiting will illustrate my invention. Example 10- A mixture of cholin chloride (1 kg.), 85 percent orthophosphoric acid (1 kg. and phosphorus pentoxide (1 kg.) was, maintained on a boiling water-bath under a pressure of 12 mm. of mercury for 5 hours. After that period the rate of esterification of cholin chloride amounted to 95 percent. The crude phosphorylation product was diluted by means of enough water (15-20 litres) for an easy subsequent filtration and in about 2 hours magnesium oxide 9 TS M MgO (750-800 g.) was added gradually while stirring, to the cold mixture so as to avoid any excess heating, and stirring was proceeded with overnight. After that period the pH-value of the liquor which should still be on the very slightly acid side was checked; the mixture was filtered to remove the magnesium hydroxide percent in my salt (reckoned in anhydrous state), instead 75 percent precipitate which was washed

pppi -q@ly a@ilo, rqpqat-

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5 edly with cold water for recovering the magnesium cholinphosphate retained by the precipitate. The various aqueous Mtrates and washing waters were joined and magnesium oxide (15-20 g.) was added thereto by small portions while following the pH-value so as eventually to obtain !a pink colour with phenolphthalein. The liquor was left standing and filtered or centrifuged until a clear liquor was obtained, then strongly concentrated under a reduced pressure at a low temperature (409 C). To the concentrated solution thus obwned ethanol (1 to 2 volumes) was added, catising crystalliz,,ttion of magnesium cholinphosphate at a low- temperature, Magnesium cholinphosphate having a betain structure, containing 14 mols of water and corresponding to the for- mul,a 0 11- (HaC)3=-N-CH2-CH2-O-P 0 Mg-14H@O 12 was dried and finally obtained with a yield of 85-90 percent, as colourless crystals grouped in clusters, which were very soluble in water and in methanol at ordinary temperature, fairly soluble in hot absolute ethanol but insoluble in acetone. Analysis: Found Cale. P=9.7% % N=4 N=4.4 Mg=3.73% Mg=3.75% H2O=38% H2O=39% ci=nil It should be noted that while it is preferred to add ethanol for an easier crystallization, such addition is not absolutely necessary for obtaining- crystallized magnesium cholinphosphate, as said cholin phosphate is capable of forming very big crystals in a suitably cooled saturated aqueo.,Lis solution. The above compound containing 14 mols of water loses 4 portion of that water upon heating even to such moderate temperatures as 40-50' C., becoming hygroscopic and slowly recovering so much water as it lost. It was found to have a very high lipotropic activity shown by pha-rmacological experiments and corroborated by clinical study. Exaniple 2-The same amount of cholin cbloride (I kg.) as in Example I was employed - and it was Vhosphorylated in the same manner. After diluting the crude phosphorylation product with the same amount of water, the product was brought under the same conditions to the same pH-value in the neighbourhood of neutrality by mean@ of calcium hydroxide (1300-1350 g.). The precipitated calcium phosphate was filtered off, the filtrate alkalinized with a small amount of calcium hydroxide (15-20 g.) and the precipitated calcium phosphate washed and isolated as described in Example 1. In this case, besides the desired calcitim cholinphosphate, a variable amount of calcium choliapbosphate cbloride was formed but being less sol.,uble in water it crystallized spontaneously as soon as the solution was colicentrated enough. The filtrate and washing licuids were joined and concentrated, placed in a refrigerator then filtered for removing @an amount of crystallized calcium cholinphosphate chloride. To the filtrate acetone (twice the volume thereof) was added causing an oily layer to separate. The mixture was again placed in the refrigerator for removing the remainder of calcium cholinphosphate chloride which is insoluble in aqueous acetonie niedium; an estimation of 3,016,399 6 The Oily layer was separated, filtered and emulsified into an equal volume of 90-95 percent (by volume) ethyl alcohol. In the refrigerator, the emulsion again formed two layers, the upper alcoholic layer containing the whole amount of nonesterified, free cholin while the lower layer contained the desired ca@Icium cholinphosphate. Left in the presence of atmospheric air the oily layer crystallized very slo@vly, yielding colourless, waxy crystals which it was difficult to isolate. The crystals were dried in vactio 10 over phosphorlis pentoxide. I thus obtained a compound showing various degrees of hydration according to the experiment; it corresponded to formula 0 15 (I-I3C) 3=-N-CHz--CI-12-0- PI, -0 Ca.nH20 I 1 -V -12 n being variable. The compound was very soluble in water, methanol 20 and absolute ethanol but insoluble in acetone. Exainple 3.-To an aqueous solution (200 ml.) containing calcium cholinphosphate (100 g. reckoned as anhydr(yus salt), a concentrated aqueous solution of COSO4.7H2O (69.5 g. in 150 ml. of distilled water) was 25 added slowly. The mixture was slightly warmed on a water-bath until incipient precipitation of CaSO4- It was then left at room temperature for 12 hours. The precipitated CaSO4 was filtered off or centrifuged 30 then washed with methanol until it became colourless. The methanolic washing liquid was added to the main aqueous filtrate, in some cases causing separation of a fur-ther amount of CaSO4- The mixture was again filtered after a rest period of 12

hours. 35 The filtrate was concentrated under a reduced pressure to remove methanol. To the aqueous filtrate 95 percent (by volume) ethyl alcohol was added by the amount just necessary to cause the filtrate to become slightly turbid. The filtrate was placed in a refrigerator and upon incipient crystallization - a further addition of ethanol was made to promote crystallization. The mother liquor then became substantially colourless. Analysis: 45 Found Calculated P=8.80% P=8.94% N=4.06% N=4.04% CO=8.55% CO=8.51% 5 H₂O=39% H₂O=39% O Cl=nil The compound corresponded to the formula C₁₁H₁₅(H₂C).s--in-CHT-ClI1-o-P-O- CO-15H₂O -12 It was obtained as pink or blue crystals, very soluble in water, in methanol and in absolute ethanol. The colour change did not correspond to any significant loss of crystallization. 60 lization water. I F, sample 4.-To an aqueous solution (200 ml.) containing calcium cholinphosphate (100 g. reckoned as anhydrous salt) an aqueous solution of ferric sulphate Fe₂(SO₄)₃ (33 g. in 300 ml. of distilled water) was added 65 slowly. The mixture was left for 12 hours at ambient temperature. The precipitated calcium sulphate produced therein was then separated by filtering or centrifuging then washed 70 with methanol until it was substantially colourless. The washing methanol liquor was then added to the main aqueous filtrate, the mixture left standing for 12 hours, and filtered for removing a further amount of calcium sulphate precipitated by methanol, then concentrated under a reduced pressure for removing methanol.

Full	Title	Citation	Front	Review	Classification	Date	Reference	Claims	NUMC	Draw. De
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12. Document ID: US 2845360 A

L2: Entry 12 of 15

File: USOC

Jul 29, 1958

DOCUMENT-IDENTIFIER: US 2845360 A

TITLE: Explosion resistant refractory castable

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United States Patent Office 2,845,360 EXPLOSION RESISTANT REFRACTORY CASTABLE Donald F. King and Albert L. Renkey, Pittsburgh, Pa., assignors to Harbison-Walker Refractories Company, Pittsburgh, Pa., a corporation of Pennsylvania No Drawing. Application December 11, 1956 Serial No. 627,567 3 Claims. (Cl. 106-104) This invention relates to refractory castable compositions to be used in furnace construction that are capable of withstanding high temperatures and which are applied by pouring, ramming, tamping, or gunning to form monolithic structures. With the discovery, several decades ago, of monocalcium aluminate cements used in conjunction with various refractory aggregates as a protective refractory for industrial furnaces, a new art developed. Essentially the art was that of constructing industrial furnaces and the like from refractory concretes by casting or pouring techniques. The new refractory mixtures became known as refractory castables. Ordinarily either the entire raw batch or the separate ingredients are shipped dry to the point of use, whereupon water is added and refractory structures are then made on the job site as by casting the desired structure. The first refractory calcium aluminate cement compositions developed were effective up to temperatures of about 2700° F. Subsequent developments, primarily directed to the cements per se, have extended the useful temperature range of those compositions to as much as 3000° F. and even higher. These developments have involved the reduction of the content of auxiliary oxides in the cements, other than lime and alumina, to the commercially feasible minimum and have also involved the use of various procedural steps in the production of the cements to obtain a product of relatively low lime content. Other refinements

that have been employed to extend the operating range of the resultant monolithic refractories have involved the careful selection of the aggregate and the minimizing of the quantity of cement in the final composition. This latter device has been dictated by the fluxing effect which the lime-containing cement has on the mixture. As the stronger castables, which are useful in the higher temperature range, have been used for a period sufficient to develop experience with them, it has been established that they are characterized by a generic defect. This defect is a propensity of the compositions to explode when first heated. It will be realized that the chief appeal of refractory castables to furnace builders is one of time saving. The mode of installation commonly is one of pouring, ramming, tamping, or gunning; consequently, large sections can be made or cast at one time. On the other hand, a heating period consuming an extended period of time to eliminate the tendency to explode may mitigate the time advantage inherent in this method of applying the refractory. Moreover, the use of careful curing or drying procedures, while possibly decreasing the tendency of explosion to some extent, has not been entirely satisfactory as a solution to that problem. By way of example, an alumina-silica castable, bonded with the high alumina, calcium aluminate cement, used to cast an electric furnace roof was dried by standing in air for two weeks. This drying was accomplished without induced heat and Patented July 29, 1958 was considered to be an ideal curing procedure. After drying, the roof was lifted into place on the furnace and heat applied. It promptly proceeded to spall itself to pieces by a series of explosions even before the desired steel melting temperature was reached. In another instance a similar castable produced with the same type of calcium aluminate cement was used to construct a burner hood for a rotary chemical drier. Upon lighting the burner, an explosion occurred within the cast refractory. The explosion was so violent that the large steel structure housing the hood was blown horizontally 25 to 30 feet with tremendous violence. Obviously it would be a boon to this art if a simple method of avoiding these hazards were to be developed. 15 It is a major object of this invention to provide a castable refractory composition that contains a calcium aluminate cement having an Al₂O₃ to CaO ratio of at least 2 to 1 by weight that resists explosion heretofore common with these compositions. 20 It is a further object to produce a non-explosive castable refractory composition according to the foregoing object simply, inexpensively, and in a manner requiring no material changes in existing production procedures. We have discovered, and it is upon this that the present invention is in a large part predicated, that the addition of a small amount of boric acid to an otherwise explodable refractory composition that contains a calcium aluminate cement having an Al₂O₃ to CaO ratio of about 2: 1 to 6: 1 by weight will provide a resulting composition 30 that will not explode upon heating. As a consequence of this discovery, refractory castables, that do not have the explosive tendencies of castables heretofore formed by using the described high alumina type of calcium aluminate cements, can be produced simply and inexpensively 35 ly, and after installation may be heated rapidly to operating temperatures without the dangers hereinbefore described. In accordance with this invention, castable refractory compositions are prepared by incorporating in a base composition, which consists essentially of a heat-explodable mixture of aggregate and a calcium aluminate cement which has the requisite Al₂O₃ to CaO ratio, a small amount of boric acid effective to inhibit the explosive characteristics of the mixture. More specifically, compositions of this invention comprise at least a major proportion of refractory aggregate, a minor proportion of the described cement, for example 10 to 50 percent by weight, and an amount of boric acid sufficient to inhibit the explosive characteristics of the base mixture. Other materials such as Plasticizers, set regulators, and the like, used in similar or related base compositions may be present if desired. Typical materials that are included in known refractory castables are set regulators such, for example, as water-soluble organic acids or their soluble salts, such as oxalic acid, citric acid, sodium citrate, and so on. Such materials may be used in the quantities that are now conventionally provided they do not deleteriously affect the explosion-resistant characteristics of the resultant boric acid-containing castable or otherwise militate against use of the resultant composition as a refractory

castable. The optimum quantity of boric acid that is to be employed in this invention is dependent upon the particular aggregate used in addition to the quantity of cement and its Al_2O_3 to CaO ratio. We have found that as little as 0.02 percent by weight of boric acid, based on the resulting refractory composition, is effective for the described purposes. We have also used as much as 1.5 percent of boric acid satisfactorily. While larger amounts may be used, such greater amounts do not usually warrant the additional expense. Based on the cement alone, a

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A range of boric acid is about 0.002 to 0.03 part of the acid per part of cement. As pointed out above, the hydraulic cements used in this invention are calcium aluminate cements having an Al_2O_3 to CaO ratio of at least about 2:1 by weight. These cements are available commercially and are additionally characterized by high purity and high refractoriness. Refractory castables supplied in accordance with this invention by use of these cements may have a useful temperature range extending to 3000° F. and even higher. The refractory aggregates useful in this invention are those which in conjunction with the described cements form a refractory mixture that will, apart from this invention, explode when initially heated rapidly to elevated temperatures of the order of, say 2000° F. to 3000° F. Typical aggregates of this nature include, by way of example, calcined or fused alumina, calcined bauxite or diaspore, aluminum silicate aggregates such as calcined clay, calcined kaolin and ground fireclay brick and high alumina brick, and lightweight or insulating aggregates such as perlite. As a group these may be spoken of as alumina-silica aggregates. In addition to aggregates such as the foregoing, there may be included other aggregates commonly included in these compositions. We have found that small amounts of uncalcined clay, or other refractory materials, do not lessen the explosion hazard nor interfere with the advantages attending the inclusion of boric acid. All aggregates are used in the conventional manner; that is, the aggregates are used in a variety of sizes determined to yield satisfactory density and strength in the resultant product. As illustrating the invention, a refractory castable composition was prepared from calcined flint clay, ball clay and calcium aluminate cement. The ball clay and cement, which were of fine grain size that would pass a 65-mesh screen, were intimately admixed with the calcined flint clay which had been ground and screened to provide appropriate grain sizes. A wet screen analysis of the resultant mixture was as follows:

Percent	-3 + 4 mesh	5 - 10 mesh	10 - 20 mesh	20 - 30 mesh	30 - 40 mesh	40 - 60 mesh	60 - 100 mesh	100 mesh +
Calcined flint clay	35	10	28	15	10	10	10	0
Ball clay	0	0	0	0	0	0	0	100
Cement	0	0	0	0	0	0	0	100
Boric acid	0	0	0	0	0	0	0	100

The calcium aluminate cement used was purchased in the commercial market and was believed to contain about one percent of sodium citrate as a set regulator. The Al_2O_3 to CaO ratio of this cement was 4.4 to 1 by weight. To test the foregoing composition for explosion tendencies, water was added thereto until a suitable ramming consistency developed. A block was then formed from the mixture with the dimensions, in inches, of 18 x 18 x 9. The block was air-dried over night, after which it was installed with an 18 x 18 inch face flush against the doorway of a gas-fired test furnace. Heat was then applied and at a rate such that a temperature of 2550° F. was attained in two hours because it had been determined that these conditions were as severe as any that would likely be encountered in commercial practice. No explosions occurred, and the cast block maintained its form without any deterioration. It thus gave evidence, later fully substantiated by experience in furnace walls, that this composition would be a refractory product of great usefulness. On the other hand, when the same test was run on a castable mix, which was identical except for the omission of boric acid, the panel exploded and the face blew off to a depth of an inch or more before the temperature of 2550° F. was reached. These results show

that the addition of a small amount of boric acid will eliminate the explosion characteristics 20 of a refractory composition that contains the described aggregates and cements. Other tests have confirmed these data. It will be appreciated that these same results may be achieved by adding the boric acid to the aggregate or cement rather than directly to a mixture of aggregate 25 and cement. According to the provisions of the patent statutes, we have explained the principle of our invention and have described what we now consider to represent its best embodiment. However, we desire to have it understood 30 that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described. We claim: 35 in 1. An explosion resistant refractory castable consisting essentially of refractory aggregate selected from the group consisting of alumina and alumina silica aggregate and a high alumina, calcium aluminate cement which has an Al₂O₃ to CaO ratio of about 2:1 to 6:1 by weight and 40 containing boric acid in an amount of about 0.02 to 1.5 percent based on the weight of the mixture. 2. A hydraulic cement for use in conjunction with refractory aggregate to produce a refractory castable, which consists essentially of calcium alumin@ate cement having 45 an Al₂O₃ to CaO ratio of about 2: 1 to 6: 1 by weight and boric acid, said boric acid being present in an amount of about 0.002 to 0.03 part for each part of cement. 3. That method of inhibiting the explosion tendencies Of a refractory castable composition which consists es- 50 sentially of refractory aggregate selected from the group consisting of alurnina and alumina silica aggregate and a calcium aluminate cement which has an Al₂O₃ to CaO ratio of about 2:1 to 6:1 by weight, which comprises incorporating in said composition boric acid in an amount 55 of about 0.02 to 1.5 percent based on the weight of solids in said composition. References Cited @'n the file of this patent UNITED STATES PATENTS 60 2,516,892 Lobaugh ----- Aug. 1, 1950 21684,913 West ----- July 27, 1954

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KMMC	Draw. Des
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☐ 13. Document ID: US 2782113 A

L2: Entry 13 of 15

File: USOC

Feb 19, 1957

DOCUMENT-IDENTIFIER: US 2782113 A

TITLE: Fertilizer compositions and method of preparation thereof

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2 @ 7 8 2 9 1 1 3 Uni'ted States Patent Office Patented Feb. 19, 1957 2,782,113
 FERTILIZE4 R COMPOSITIONS AND METHOD OF 5 PREPARATION THEREOF Grover L. Bridger and
 David R. Boylan, Ames, Iowa, assignors to Iowa State College Research Foundation,
 Inc., Ames, Iowa, a corporation of Iowa Application March 8, 1952, Serial No.
 275,578 io 2 Claims. (Cl. 71-47) This invention relates to fertilizer compositions
 and 15 method of preparation thereof. The met@hod of this in- vention has
 particular utility in preparing novel fertilizer compositions from phosphate @rock
 and lan,-beinite. The method of this invention can also be advanta,@eously ap-
 plied to the preparation of fertilizer compositiolis from 20 phosphate rock and
 magnesium sulfate, or from phosphate rock, ma.-nesitim sulfate, and potassium
 sulfate. Phosphate rock oT apatite is a sedimentaty roak- con- taining calciuni
 phosphate found in very large deposits throu.-hout the world. The chemical formula
 of the 25 main constituent of phosphate rock is generally given as 3Ca(PO4)2.CaF2.
 As can be seen from this formula, the primary constittient!of phosphaterock is
 actually calcium fluorophosphate. Finely ground phosphate rock is used directly as
 a fertilizer for supplying phosphorus, which 30 is a major nut-ritional requirement
 of most plants. T@he p-hosphortis content of phosphate rock, usually expressed as

percent of phosphorus pentoxide (P₂O₅), is practically insoluble in pure water. However, the phosphorus is gradually brought into solution by the slightly active acids in the soil. This process requires considerable time, and plants lacking the advantage of branching root systems are not able to take adequate advantage of the phosphorus in phosphate rock. It can be seen from the above that there is a need to make the phosphorus in phosphate rock more readily available. The method which has heretofore been most generally employed for accomplishing this result is to treat the phosphate rock with sulfuric acid to form superphosphate. Superphosphate contains the phosphorus in a much more soluble form, which is generally assumed to be mostly as mono-calcium phosphate. The actual process for preparing commercial fertilizers from phosphate rock as it is generally practiced today is somewhat more complicated than indicated above. The usual process consists of the treatment of phosphate rock with sulfuric acid to form superphosphate as set out. The superphosphate is then cured or dried for several weeks during which period it must be stored indoors, and thereafter it is mixed with other materials such as potassium chloride or ammonium nitrate, depending on the desired plant nutrients either as solids or in solution. The mixed product is subsequently dried, pulverized or granulated, and shipped in suitable containers, which are generally fiber or cloth bags. The disadvantages of this commercial process for preparing fertilizers from phosphate rock can be set out as follows:

- (1) The acidulation of the phosphate rock with sulfuric acid increases the cost and difficulty of preparation of the fertilizer.
- (2) Considerable time is required for curing or drying the superphosphate, which requires large storage buildings, and a considerable inventory tie-up.
- (3) The superphosphate product generally has a marked acidity, which in turn causes bag rot in the packaged fertilizer product.
- (4) Other chemicals must be added to the superphosphate to supply the major plant nutrient potassium, and secondary plant nutrients such as magnesium and calcium must be separately supplied to the soil. Langbeinite is obtained in large quantities as a byproduct in the recovery of sylvite (KCl) from the Permian salt beds occurring near Carlsbad, New Mexico. Langbeinite is a double salt of potassium sulfate and magnesium sulfate in the ratio of one mole of potassium sulfate to two moles of magnesium sulfate. Its formula can be written as K₂SO₄·2MgSO₄. Langbeinite is presently processed for the production of potassium sulfate by reacting the langbeinite with potassium chloride. The byproduct of this reaction is magnesium chloride. As indicated above, both phosphorus and potassium are important elements for plant growth. These elements are generally thought of as being used by plants in the form of their oxides, for example, as P₂O₅ and K₂O. It is generally agreed that phosphoric acid or phosphoric pentoxide and potash or potassium oxide are major plant nutrients. Most plants also require magnesium and calcium as secondary plant nutrients, and a lesser amount of sulfur. There are also other elements which are important in the nutrition of plants in greater or lesser amounts, but the elements mentioned are those with which the present invention is primarily concerned. It is therefore a general object of this invention to provide a new method of producing fertilizer compositions from phosphate rock, which substantially overcomes the disadvantages of the superphosphate process set out above, while at the same time producing novel fertilizer compositions in which the phosphorus is readily available, and which in addition supply other plant nutrients such as magnesium, calcium, sulfur, and if desired potassium. It is a more specific object of this invention to provide a method of forming novel fertilizer compositions from phosphate rock and langbeinite which are characterized by high phosphorus availability. It is a still further object of this invention to provide a method of producing highly effective fertilizer compositions from phosphate rock and magnesium sulfate, or from phosphate rock, magnesium sulfate and potassium sulfate, all of which fertilizer compositions are characterized by high phosphorus availability and also by supplying magnesium and other nutritional elements in addition to phosphorus. Further objects and advantages will appear as the specification proceeds. The general method of preparing the fertilizer compositions of this invention is centered around the important step of bringing about a heat fusion of a mixture of phosphate rock and the indicated metallic sulfates (magnesium, or magnesium and

potassium sulfates). This step can readily be accomplished by feeding a mixture of controlled proportions of phosphate rock and the metallic sulfates into a suitable furnace wherein the minerals are melted and fused. Preferably, the raw materials are ground and thoroughly mixed before charging, and introduced into the furnace in an agglomerated form. The temperatures required to bring about the desired heat fusion of the phosphate rock and the metallic sulfates is generally within the range from about 2000 to 2500° F., although somewhat higher or lower temperatures can be employed if desired. The fused mass of phosphate rock and mineral sulfates is then rapidly cooled. Preferably, the hot fused mass of minerals, which may be at a temperature considerably above 2000° F., is cooled rapidly by quenching the molten mass in a suitable cooling medium, such as a stream or bath of water, steam, air, etc. Best results are obtained by employing a liquid cooling medium which will substantially dissolve the product. The preferred liquid cooling medium is water saturated with a salt or mixtures of salts providing common ions with that of the fertilizer composition, such as potassium ions, magnesium ions

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2,782,413 sulfate ions, etc. Langbeinite, or a mixture of magnesium sulfate and potassium sulfate are excellent salts for use in substantially saturating the aqueous cooling medium. When the molten mass of minerals is rapidly quenched, for example in water substantially saturated with langbeinite, the molten mass as it is cooled breaks up into granules. Rapid cooling of the fused mass is believed to be important in maximizing the availability of the phosphorus. This can be done most conveniently in a liquid cooling medium, since the melt is quickly broken up into small particles in the medium. The particles or granules can be separated by filtration, and used directly as fertilizer. If desired the granules can be subjected to a pulverizing operation to reduce the particle size. As a specific example of the present invention, the following may be set out: 100 parts by weight of phosphate rock containing 32.5% P₂O₅ was mixed intimately with 187 parts by weight of langbeinite (K₂SO₄·2MgSO₄). The mixture was melted in a gas-fired furnace at 2200° F., and quickly cooled by quenching in a saturated aqueous solution of langbeinite. The product from the quenching operation was in granular form and was separated from the quenching solution by filtering. The granulated product was milky in appearance and quite soft. It was dried to remove moisture, and was then ground for immediate use in proportions above about 120 parts by weight of langbeinite to 100 parts of phosphate rock the fertilizer compositions may be said to be characterized by high phosphorus availability, and therefore to be of considerable commercial importance. When 180 parts by weight of langbeinite or greater are fused with 100 parts by weight of phosphate rock as preferred, substantially all of the phosphorus in the resulting fertilizer composition is readily available, as indicated by the flat portion of the curve running substantially parallel with the 100% availability line on the graph of Fig. 1. Mixtures of potassium sulfate and magnesium sulfate in the same proportions as in langbeinite will give the same result when fused with phosphate rock. In addition, it has been discovered that other proportions of potassium sulfate and magnesium sulfate can be employed, and that magnesium sulfate alone may be used. The results of fusion studies of the three component system, magnesium sulfate-potassium sulfate-phosphate rock are reported in Table 11, and the data of Fig. 2 have been used to plot the three component diagram of Fig. 2. Table II.—Results of fusion studies of the three component system, magnesium sulfate-potassium sulfate-phosphate rock. use without further storage or treatment. The chemical formulae for the availability of P₂O₅, CaSO₄, and MgSO₄ are given. Total (C) is the composition of the product thus produced is given in Percent. Percent P₂O₅, P₂O₅ Table 1. 30 Percent P₂O₅ Table I.—Analysis of typical fused fertilizer—H—1—12 48 40 4.4 13 1 33 from langbeinite-phosphate fusion G—1—14 56 30 1 4 . 0 7'8 E-2—20 30 50 C, 12.0 D-2—24 36 40 2 1 12.4 Total, Soltib C-2—28 4 2 30 8. 0 1 10. 3 8 (le, 3 5 B-2—32 4 8 20 7. 9 Percent Percent 18, 0 99 1-3—29 21 50 75 6. 8 16 D-3—34.8 25.2 40 13.3 13.8 96 P₂O₅ 13.8

13.3 C-3--- .-

 40.6 29.4 30 II. 9 11. 2 1 (1) K20 -----
 ----- 13.0 b 12.4 B-3----- 46.4 33.6 20
 7. 4 7.,! io(mgo ----- 11.5 10.9 E-4-----
 37.5 12.6 50 le). 9 1-. (I @)9 F 1.6 D-4 ---- 45 15 40 14.6 14.6 i(O 40
 G-4 ---- 52.5 17.5 30 1(.0 10.0 lo(--- B-4 -- -- 60 20 20 7. C,
 7.2 i(O Solubility in 2% citric ,acid. F-5----- 40 ----- --- 60 16:2 2 78 'o b
 Solubility in hot water (Association of Official Agricultural Chemists 50 17 4
 E-5----- so ----- IS 0 96 procedut,c). B-5 ----- 80 ----- 20 C). 30 6.20
 I(O For the purpose of preparing fertilizer compositions of A-5 ----- 90 -----
 10 3.40 3. 3r, If(high phosphorus availability from phosphate rock by the 4 i-) -
 Percent by weight. method of this invention, it is important to control the
 proportions of phosphate rock to the metallic sulfites, and particularly to ma-
 gnesium sulfate. Langbeinite is the preferred source of the sulfates of potassium
 and magnesium because of its cheapness and availability. @5 0 Wien- langbeinite is
 used to prepare the fertilizer compositions, at least 120 parts by weight of
 langbeinite should be fused with each 100 parts of phosphate rock. Preferably, at
 least 180 parts by weight of langbeinite should be fused with each 100 parts by
 weight of phosphate rock. The reasons for these limitations on the weight ratios of
 langbeinite to phosphate rock are indicated clearly in Fig. 1 of the drawing. Fig.
 1 is a graph showing the effect on phosphorus a@/ailability (as P2O5) of varying
 the number of parts by weight of (iO langbeinite per 100 parts of phosphate rock.
 The fusion compositions of langbeinite and phosphbate rock upon which the curve of
 the graph in Fig. I is based were produced in accordance with the process set out
 iii the specifitc example above. The phosphorus availability (as P2Os) was-
 determined by the standard availabil;ty test using 2% citric acid. It will be noted
 that about 69% of the phosphorus in the fused fertilizer compositioii is readily
 available when 120 parts by weight of langbeinite are fused with 100 parts by
 we:light of ph6sphate rock. When less than 120 parts by weight of langbeinite are
 fused with 100 parts of phosphate rock, the phosphorus availability falls off
 rapidly, and the product thus produced would not appear to be of conimercial
 importance as compared with superphosphate. However, Original Conip.1, Prodtict
 Conil), ---i On the basis of the figures set out in T,,ible It and pL@rticularly on
 the basis of the three componeit diagrini of Fig. 2, it can be seen that the
 proportions of phosphate rock, niagesium sulfate, and po',assiuni sulltte cail be
 varied considerably while produciig a fused fertilizeicomposition of high
 phosphoi-us availabilit@,. The area of high phosphorus availability is labeled on
 th@- three coi- nponent diagram of Fig. 2 and is bounded by @i sojid relatively
 heavy line. The numbers in parentheses on the diagram of Fig. 2 indicate the
 percent of the P2O5 ill I]IC fer0lizer product which is soltible in 2@'o citric
 acid, ind correspond with the values appe,,iriig opposite the corresponding fusion
 code numbers in Table JI. The points, on the three component dia.-ral-n Df Fig. 2
 f,,,iling within the area of high phosphorus availabil;ty iilciuding the points
 falling on the boundary line all reprcseilt possible fertilizer compositions which
 substantially tchieve the objects of this invention. ll, will 1)e uiide,-stc)od
 tli@it each point on the three compopent dici.@riiii (f Fig. 2 posil vely fixes the
 proportions of the three ingredients of the ftisecl fertilizer composition to eph
 other, that is, !lie i-clative proportions of phosphate roc'&-, ,)otissium !
 itilfpte, "in@ magnesium sulfate, Since the pi@ii-pose ol- tjie present iiventiou
 is to prepare fertilizer coi-nposition froni phosphate rock, the area of high
 phospliorlis aviillabilit@, (if Fi@@. 2 has not been indicated as extending I)efow
 conip'osi'tions containiing less than 10% by @k,eiglit of niiosphate rock. However,
 this does not iillean thit substanti@illy complete phosphate availability :s not
 obtained for tile total area filling under the curve foriiling the ijpper boLin([-
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Full	Title	Citation	Front	Review	Classification	Date	Reference	Claims	NUMC	Draw. De
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14. Document ID: US 2724648 A

L2: Entry 14 of 15

File: USOC

Nov 22, 1955

DOCUMENT-IDENTIFIER: US 2724648 A

TITLE: Method of processing citrus pulp

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'tr s wa 9 w@erei'n the ci u ste is@first ground to relatively small particles in a grinding apparatus such as a hammer mill. If desired, the step 2 may be performed by the washing of the small particles obtaine@ from the grinding step 1 to obtain a water extract of the free citric acid, however, this water extracting step 2 is not necessary m this process although @as will be expla'med later, the water extract obtained in this step 2 may be subseq@iently used. Preferably the small particles Will be treated after the grinding stop I v@,ith lime, CaO and $\text{Ca}(\text{OH})_2$, or other suitable alkaline reagents which includes for example the oxides and hydr,oxides of the alkaline earths including barium, magnesium and strontium, in addition to the calciurn. it is likewise true that s@its such as chloride, carb ate, and bi-carbon@te of the alkaline I earths also work in this process, and in the case when such salts are used some alkali or liydroxide should be used in conjunction with them. The lime or alkaline treatmenf in step 3 facilitates the realldy separation or dewatering step 4 which May be performed b@, using either the presses or the drainage bins as Previously explained in connection with the prior art. Whether or not the pressing method or the drainage method is used as the step 4, will det,ormine the extent of separati6n of the citrus Waste into a pulpous portion and a peel liquor portion as has been p:reviously explained. 'Ibus the pulpous portion indicated as passing to the stage 5 on the flow sheet will be i)@rt@ally dehydrat@d at this stage. In some instances the step 5 of transferring the pulp to its indicated point for subsc@quent dehydration by the s,tep 6 may be eliminated and in th@at case the alternate direct feed step 5A froin the dewatering step 4 will be carried out directly to the ammoniation step@ t2. If it is desired to t,c) tally dehydrate the citrus pulp, then the pulp can be taken from the step 5 to the dehydration step 6. The dehydr@ition step 6 can be carried out in 4ny of the known dehydration appar @atus, such@ as, for example, direct fired kilns or steam kilns. i7he res@lting product from the dehydration step 6 is a plain citrus pulp 7 which has been totaffy- dehydrated. It will be appreciated, of]-se, cou. that the extent of the dehydration will be determined by the length bf time and temperatures used largel Y, so that the plain citrus pulp indicated, as step 7, in some instances may not be entirely totally dehyd@ated, but it is Preferably carried to a moisture content of 10% or less. The peel liquor 8, obtained from the dewatering step is evaporated iii s ' tep 9 and the evaporation is preferat)ly carried out]by usin.- the submerged combus;tion pro(,ess of the patent Burdick and Allen, above referred to, and then finally evaporated to the de@ired c'o-ncentration with standard multiple-effect evaporators. The resiilting product from the evaporatioii step 9 is the plain citrus riolasses 10. @Fhtis, the process @ as outlined by the flow sheet of Fig, I v@rniit@ ihe manufacture of the plain citrus ptilp 7 and the plain citrus molasses 10, which product may be later combined with the ammoniated citrus pulp and ammoniatcd citrus molasses io obtain a r)rotein coiitei-it of a desired quantity. An ammonia siipply is provided at 11 and this @am'm'onia is fed to the ammoniator aot)aratus to carry out the ammojii@tion step 12 on either the pillp as it coines from the dewatering step 4 or on the plaiiii citrus pulp 7. The aminonia 11 is afi anhydrous amiiioinia and is preferably fed to the ammo I niator avparatiis in gaseous form. 'Ehe ,i large p essure cylinder ammonia is ordinarily stored in , r under abotit 100 to 200 pounds pressure, depending iipon its temperatiire. Liquid ammonia is metercd out through a pressure resisting valve to aboiit two pou@ds m

pressur4,. This liqliid am onia is then vaporized by passing throurl-i a beat exchanger and finally introduced into the ammoniation apparatus where the pressure is essentially atniospheric or at most a few inche@ of water pressure. Although the @g4seous anhvdrus ammonia is ordinarily used iiii the process of this invention it is irtic that since the preferred operational piessures are within a r4fi@6 of from atmospheri 'c to abotii 5 . l j6undg guage pressure that due to the vapor pressure of the liquid ammonia, the liquid aiiimonia will at the temperatures of operation of the animoniation step vaporize Avithin the ammoniation ai)i)aratus so that in effect a -E-,seous anhydrous ammo ia resu ur moniation step. Due to the vapor pressure of ammonia at the higher temperatures used in this process it would be necessary to use a high presstire in order to haie the 10 reaction proceed with liquid ammonia and to prevent its vaporizatic)n, but one of the great advantages of is inventio.1 is that the process can be carried out at substantially atmospheric pressure so that expensive super atmospheric equipment is not required. i,@ The ammoniation apparatus used in this invention may be of the batch feed type, such as described in the U. S. patent ipplication, Serial No. 250,357, above referred to, or it @-nay be in the continuous ammoniation apparat@is illustrated soniewhat diagrammatically in Fig. 2 of 20 the drawing, To minimize loss of armonia, the citrus pulp is fed into the star feeder 30, which is essentially a star shaped rotating paddle 31, Nvwhich is actually mount- ed in a cylindrical housing 33. The citrus pulp passes from the star feeder 30 int6 the first ammoniator 35, 9,@ @vwhich is made Lp of a cylindrical type section 36, having mounted therein a shaft 38 which is rollated through a chaiiii driven sprocket 40 connected thereto within the pipe section or cylinder 36 and located on the shaft 38 a.- e feediig paddles 42, which are set at an angle to the 30 shaft 38 so as to effect the horizontal movement of the citrus pulp through the ammoniator as@ indicated by the arrow therein. In some instances it may be desirable to 9 pre-heat the citrus pulp prior to addin the anhydrotis ammonia. This pre-heating can either be accomplished 35 by taking the citrus ptilp from the dehydration process diroctly so that there is a residual heat within the pulp, but in some cases the citrus ptilp will necessarii'y be stored and permitted to cool prior to ammoniation step and therefore it is possible to heat the citrus pulp 40 by tising a steam chest 44@ If the additional heating by steam chest 44 is not used in the process, then the an- hydrous amnionia l-nay be added in the first an-tmoniator 35 and iri some cases inay be added even thotigh the steam chest 44 is I required, but in the apparatus as illustrated 4,5 in Fig. 2 the citrus pulp passes fr6rn the first amm@ oniator 35 to the second a-n- imoniator 45 through a pipe 47. In the second ammoniator 45, the paddles 42 on the shaft 38 driven by a chain driven sprocket: 40 are used in the same manner as in the first ammoniator 35 @,vith 50 the horizontal movement of the citrlis pulp being in the opposite direction from that used in the ammoniator 35. Anhydrous ammonia is introduced into the second ammoniator 45 through the manifold 50 so that distribution of the ammonia is obtained throughout the am- 55 moniator 45. The paddles 42, since they are set at an angle and may constittite numerous paddle units, serve not only to provide the horizontal movement, but in addition will cause a lifting and mixing action on the citrus pulp so that adequate surface contact of the an- 60 hydrous amnio,nia with the citrus pulp is obtained. At the end of the ammoniator 45 is a secoiid connectin,@ pipe 51 which feeds into the third ammoniator 55, which is of similar construction to the second ammoniator 45 having the paddl.- 42 on the I shaft 33 operated by the chain 65 driven sprocket 40 and providing a horizontal movement in the same direction as that obtained in the first ammopiator 35 Likewise, the anhydrous ammonia is fed throu--h a m ! anifold 50 as in the second, ammon--'at6r 45, At the discharge end of the third ammoiiiator 55 is a 70 second star feeder 60 which is of identical constriction with the star feeder 30 used for introducing the citrus pulp, and likewise also prevents the loss of ammonia from the apparatus. Actually the continuous ammoniator apparatus of Fig. 2 is preferably gas tight or at least semi- 75 gas tight to preve I nt the loss of ammonia thr oughout,

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2,724,648 7 However, expensive pressure equipment which would be necessary if the

process were operated above the atmospheric to 5 pounds pressure range preferred in this invention is not necessary. The chain driven sprocket 40 and the star feeders 30 and 60 are synchronized by a 5 chain drive or similar drive so that they are operating at a predetermined desired rate of speed. After the ammoniation step 12 there is still present in the ammoniated citrus pulp some free or unreacted ammonia. This free or unreacted ammonia give out not only a product of undesirable odor, but would also be harmful to ruminants if fed as such and finally unless utilized the loss of ammonia would be wasteful. In order to de-ammoniate the ammoniated citrus pulp, that is to remove or chemically change the free ammonia within the ammoniated citrus pulp so as to prevent the above enumerated disadvantages of its presence, the de-ammoniation step can include the passing of air or flue gases or carbon-dioxide over the ammoniated citrus pulp. When the variation of the method of employing a gas is used, the free ammonia will be removed from the citrus pulp while when treating with the flue gases or carbon-dioxide gas there will be formed ammonium carbonate and/or ammonium bicarbonate, both of which are utilizable by ruminants as a source of protein as well as being usable for fertilizer. However, in the process of this invention it has been found that the preferred method of eliminating the disadvantages of the excess uncombined ammonia from the ammoniated citrus pulp is by the addition on to the ammoniated citrus pulp of a non-toxic acidifying agent like phosphoric acid and its acidic salt of potassium or calcium. When using the phosphoric acid or its acidic derivative the uncombined excess ammonia in the citrus pulp is neutralized in addition to increasing the phosphate content of the citrus pulp which is desirable in order to make a balanced feed and which is also suitable for increasing the general content of fertilizer. If desired, other non-toxic acidic material can be used for combining with the free ammonia, for example, citric acid is a suitable acidic material for this purpose. After the ammoniation step 12 and if desired after the de-ammoniation step not shown but above described, the extraction step 13 is carried out. Ordinarily however, in this invention one of the advantages presented is that the de-ammoniation step is not necessary after the ammoniation step 12 because it can be combined with the extraction step 13 as will be described hereinafter. The extraction step 13 is carried out by the addition of an extracting medium to the ammoniated citrus pulp obtained by the ammoniation step 12. This extracting medium can take various forms but the main purpose of the extraction step is to extract from the ammoniated citrus pulp a portion of the nitrogen content imparted thereto in the form of "synthetic protein" or "substitute protein" which has been added over and above that originally present in the citrus waste by the ammoniation step 12, as an example of the extracting medium which can be used in the extraction step 13, the water extract of the free citric acids obtained after the grinding step 1 as indicated on the flow sheet can be used, in which case a portion of the "synthetic protein" present in the ammoniated citrus pulp will be incorporated with the water extract 2. Also the peel liquor obtained in step 8 as shown on the flow sheet or a mixture of the peel liquor 8 and the water extract 2 may be used as the extracting medium. Whatever extracting medium is used, the medium should be acidified so that the pH after mixing the extracting medium with the ammoniated citrus pulp will be adjusted to 7 or lower, and preferably within a range of 5 to 7 inclusive. This adjustment of the pH below 7 is necessary to prevent loss of ammonia through decomposition or volatilization. The acids which may be used for the adjusting of the pH are, for example, any non-toxic acidic material like phosphoric acid, carbonic acid, citric acid, acetic acid, and the calcium and potassium salts of these acids. As previously mentioned in connection with crystallization of the excess uncombined ammonia, the use of phosphoric acid is particularly desirable because it raises the phosphorus content of the ammoniated product. It should also be pointed out that a citrus molasses can be made from the dehydrated citrus pulps alone without the use of the peel liquors as the extracting mediums, for example, in the Example 4 which follows herein, water alone was used as the extracting agent. The extraction step may be carried out, in an apparatus of the type illustrated in Fig. 2 which is shown as an

extracting -,tpparatus 65. Thus ttle ammoniated citrus p,,Ulp are fed.fr6m the star feeder 60 into the extracting ap ,paratus 65 at the ri-@ht hand end 6f: a cvlinder 66 as shonvn in Fig. 2 withiri the extracting.cylinder 66 may be loca@ted a screw type conve-Yer or similar mixing device 68 whi6h moves the solid pulp to the l(@ft of the sheet of drawing. The peel liquors are preferably -added through an inlet pipe 70 at the opposite end of the c3llinder 66 from -the Star feeder 60 so that there is a countermo,,rement Of the citrus pulp and the peel liqljors or other extraction medium entering through the inlet pipe 70. The screw conveyor 68 is located in pbsition on a shaft 75 which is operated by a chain dn'ven sprocket 76 ,vhich if desired, may be connected with the chain,driven sprocket 40 and;the star feeders 30 and 60 for synchronization, although this will not be necessary. The ammoniated liquors di-ic to the tilt of the extracting ap,,paratus 65, as shonvn in Fig. 2 ivill drain from ihe righthand end of the extractor 55, w@llereas- the ammoniated ptil _p w H exitthrou,gh an outlet.pipe 78. As the ammoniated liquors are discharged at -the lower l6vel 80, a screen m4y be used at'80 to prevent the solids from passing cut o'f the dischai7ge openina 80 along with the ammoniated c)@tracting medium or liquors. 'It should be pointed otit that 'in the ammoiiiation step 12, that the amo,,int of anhydrous ammonia added per unit of @citrus pulp during thatstep will determine largely 'L'he amount of "synthetic protein" produced. Also, the amount of 'the "synthetic protein" which is incorporated with the extra-,ting medium can be varied.and controlled by varyipg and controllin,@ 7the vollime of the extracting liquor or mediuni as will be apparent from Examples 5 and 6, Vhich followherein; also, the particiiaar extract:.n.@ medium being used will determine to sotne extent the amount of "synthetic protein" which is incorporat,-d with the extractiilig mediurn and the amount which is left in the,ammoniated ditrus piiLD. Ordinarily after the ekstracting st(@p 13 the slurry t.)rod.,uced in'that extracting step .13 will be deW4tered by e.;ther the pressing method or the draina,-e method prviously described aid as Nvas cari:ied olit in step 4 of this process as shown in Fig' 1. This second dewatering 14 is more readily acco-pplislied than he first-.dexvaterin- 4 since the ammoniation in tep 12 t s seems to eliminate inore of the colloidal and gel-like properties of the citrus peel. The deivatering,operation 14 produces ammojiated citruis piiLP stream 15 and an ammoniated iquor stream 18. However, the amount of each which is contained can be controlled by the amount of the extracting mediunis used as well as by whether @or not the dewatering step 14 is ii,-ed, as will be rendered apparent when a comparision of the Examples 7 and 8 which Lre set forth herein. Thus, it can be seen from the Exa-ple 7 Which f-61]ows that when a smail volume of the extracting medium or liqubr wis used all of the "synthetic protein" and- the entire pr6duct in fact was in the form of ammoniated citrus ptilp, v@n- @reas, in Example 8 which f-cillows it caii be seen by using the dewatering step, more of the "synthetic,protein" is made to appear in.the ammoniated citrus liquor or ar-imoniated molasses. The ammoniated citrus pulp can be dehydrated in step 16 in a manner sinlilar to that en-iployed in step 6 to thus produce the fi-nal ammoniated c;trus pulp 17 iihich contains the "-,ynthetic protein" or ilitrogen niaterial which is avail-

Full	Title	Citation	Front	Review	Classification	Date	Reference			Claims	KnowC	Draw. De
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L2: Entry 15 of 15

File: USOC

Mar 3, 1931

DOCUMENT-IDENTIFIER: US 1795173 A

TITLE: Process of rendering insoluble phosphates available

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Patented Mar. 3., 1931 1 9 7 9 5 p 1 7 3 UNI:TED STATES PATENT OFFICE H'S LEMMOKE, OF 7 RANKFORT-ON-THE-XAIN, y PROCESS OF P.ZNDERMG INSOLU33LE PHOSPHATES AVA3[LA33LE No 1]rawing. Application:filed Zanuary 28,2929, Serial No. 3,35,731, and in Germany - Tanuary 26,1928. This invention relat es to a process iDf renderin& useful, inisoluble phosphates, par- ticularly@-natural mineral phosphates, and for which I have filod application in G6r-' rnany, January 26, 1928. In renderiia g us6ful the phosphorus conteiat of iiisolitble phophates such as for example natural mineral phosph;ites, by heating saicl phosphates With suitable additions,' 10 for exelmples, for the purpose of producing an easily assimilable fertilizei'tit was hitherto customary either to transforin the entire phosphorus content o-f the initial material in the molten or sintered decompo ition product example into so-called calcined phosphates, or the like, or to remo-ve the entire phosphorus content. from the initial materia-Is by treatin same with reducing agents and other 9 20 suitable additions and drivmg 6ff the phosphorus formed, in which latter case the phosphorus distilling over *as transforitied into pyosphoric acid by burning. for example.with air, or into another water-soluble form, for 25 example into monocalcium. ph@@phate or ihe lilfe, and the residual slag was either thrown to waste, or worked u@p i.nto bricks and, similar products. Since th6]Vortions of phosphoric acid remaining in th&se residues were thus 30 rendered unavailable for recovery ajid utilization7 it was necessa@y to take care to ensure that the amounts thereof were kept as low as ' c that is to say that as much phos- ssibl, , Pho olus p p or. phos horic acid as possible - was 35 driven off from the initial materials during their decomposition. This however entails not only an excessivi-,Iy long duration of the decomposit.ion process, but aIsG the employment of disproportionately. high tempera- 40 tures and thp, consumption of larcre amounts of fuol whilst simultancousl@ t)t@e material of the furn@ce is subjected to extremely great acting mass. i invention the" ad- 45 operation are so selected that only a ipart, for example ab6ut i r, intothecitricacid-orcitate-solubleform,for'bilityin@itricacidorcitratesolution. Thus or acid, whilst the remainder in the slag is transformed into a citric acid- 'or citrate-soluble form. - It is thus possible to utilize the total phos- phoirus content of the initial material to the 55 gr@atest possible extent whilst greatly,.economizing in fiel and greatly decreasing. wear on the furnace material, at considerably lower temeperatures in a -very short time which generally amounts to about one half 60 of that required in the known processes. - ' The co'nditions are advantageously so selected that the slag obta@ined has the composition of a silico-phosphate of optimum solu- for example it may be a silico-phosphate of the formula $(CaO),, .P, .05.SiO, .$ It is ho-w- ever within the scope of the invention to pro- duce a slag of a composition differing from this formula. The additional substances 70 which are suitable for use comprise every type of carbon, for example ground coke, or carboni ferous substances, earboniferous waste prod.u cts of all kinds @nd the like and silica of any type. 75 The amount of carbon or carboniferous additio ns to be employed is -equivalent to ilie amount of phosphorous whicli it is desired to obtain by. drivino, Off, ttnd is generary so adjuste d ihat.ab6it 5 atoms of carbon are em- 80 ployecl per molecql-e of phosphoric acid to be reduce (f, in ace@ordance with the equat'ion: $P_2O_5 + 5C \rightarrow P_2O_4 + 5CO$. The total amount of carbon may for ex- s5 hinple I)e such that abolit 25-55 % (advan- tageou sly about 50--55,7o) of the available pliospli ortis is converte.d into a volatilized The proportion bywei (rlit of the silica to i)o the pliospil.orus I)ciitoxid-c preseit may be selected, iii the residiial slag, for example to corres ond to the foregoing formulit i. e., about 0.42 and the ratiq of uaO to P_2O_5 , may be selected to be about 1.97.. Accordingly if 95 only about one half of the phosphorus,pres- statl@. I 50 .to 55@'o of the total phosphorus present. ent is to remain behil@d in the slag, the in'the initial material is dri-ven o:ff as such amounts of the added substances must be for recovery in a water-soluble form and so adjusted that in the oiiginal-mixture the r'o transformed for e:kample into phosphoric proportion by weight of SiO_2 : P_2O_5 amounts loo

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1,795,178 to about 0.21 and the ratio $\text{CaO} : \text{P}_2\text{O}_5$, to about 0.99 in which case any excess lime which may be present in the raw phosphate must be taken care of by a suitable addition of silica, advantageously in such a manner that the lime is transformed into calcium orthosilicate. Moreover no undesired losses of phosphoric acid need be feared even when employing an excess of silica, since any phosphoric acid liberated by the excess silica cannot generally distil over at the relatively low operating temperatures which come into consideration. Temperature of between 1000 to 1400° C. and primarily between about 1250 to, 1400° C. have proved suitable as operating temperatures. By way of example, by calcining a mixture of about 100 parts of a raw phosphate (containing 36% P_2O_5 , 67% SiO_2 , and 47 to 48% CaO) with about 7 to 10 parts of carbon and about 8 to 10 parts silica at 1200 to 1400° C. and after driving off about 50 % of the total phosphorus contained in the raw phosphate employed, a calcined residue is obtained which contains the remainder of the phosphorus, the bulk of which is in the citric acid soluble form and constitutes an excellent fertilizer, whereas the expelled phosphorus can be transformed in known manner into phosphoric acid by burning for example with air and furthermore, into any desired other products which may for example likewise be used as fertilizers. When employing phosphates which per se contain less than the required amount of silica, it is possible to add the silica also wholly or partly in the form of phosphates richer in silica instead of adding the silica as such. Instead of bringing the calcined product after cooling into the finely powdered form in which it is required as use for a fertilizer, for example, by grinding or the like, the still hot calcined residue may advantageously be quenched with water or with suitable solutions such as a raw potash salt solution, for example by introducing the same into water or into such solutions or spraying the solutions on to said product for example, in a cooling drum provided with a suitable spraying device, in which case a very considerable comminution can be attained on occasion with a simultaneous hydration of the product. The term "carbon" employed herein and in the appended claims is intended to denote any carbon-containing substance of any kind and particularly all kinds of fossil carbon, coke and also coal and any waste products containing carbon in any form whatsoever. Like, wise the term "silica" (SiO_2) employed here, in and in the appended claims is intended to comprise all types of silica and also acid silicates as well as products containing silica as such or in the form of acid silicates, for example waste products. Claims- 1. A process of rendering useful insoluble phosphates, which comprises heating substances containing insoluble phosphates at temperatures of from about 1000-1400° C. with such amounts of carbon and silica-containing additions that a part of the total phosphorus content of the initial material is liberated by the carbon in accordance with the equation $\text{P}_2\text{O}_5 + 5\text{C} = \text{P}_4 + 5\text{CO}$ and that in the calcined residue containing the other part of the phosphorus the proportion of the constituents P_2O_5 , SiO_2 , and CaO is about 80 0.9-1.1 molecules of P_2O_5 , to about 0.9-1.1 molecules of SiO_2 , to about 4.8-5.2 molecules of CaO . 2. A process of rendering useful insoluble phosphates, which comprises heating substances containing insoluble mineral phosphates at temperature of from about 1000- 1400° C. with such amounts of carbon and silica containing additions that a part of the total phosphorus content of the initial material is liberated by the carbon in accordance with the equation $\text{P}_2\text{O}_5 + 5\text{C} = \text{P}_4 + 5\text{CO}$ and that in the calcined residue containing the rest of the phosphorus the proportion of the constituents, P_2O_5 , SiO_2 and CaO is about 95 0.9-1.1 molecules of P_2O_5 , to about 0.9-1.1 molecules of SiO_2 , to about 4.8-5.2 molecules of CaO . 3. A process of rendering useful insoluble phosphates, which comprises heating substances containing insoluble phosphates at temperatures of from about 1000-1400° C. with such amounts of carbon and silica containing additions that about 25 to 55% of the total phosphorus contained in the initial material is liberated by the carbon in accordance with the equation $\text{P}_2\text{O}_5 + 5\text{C} = \text{P}_4 + 5\text{CO}$ and that in the calcined residue containing the rest of the phosphorus the proportion of the constituents P_2O_5 , SiO_2 and CaO is about 110 0.9-1.1 molecules of P_2O_5 , to about 0.9-1.1 molecules of SiO_2 , to about 4.8-5.2 molecules of CaO continuing the heating until the desired amount of phosphorus will be distilled off 't'hereupon crushing the

calcined residue 115 in a known manner to the fineness required for its further use. 4. Process of rendering useful insoluble phosphates which comprises heating insol- ule mineral phosphates at temperatures of 12(1 about 1000-14000 C. with such amounts of carbon a4d sieca as are required to liberate about 20-55% of the total phosphorus con- tained in the iiiitial material in accordance with the equation $PO_4 + 5C = P + 5CO$ and 125 to ensure ihat the compo@ition of the result- ant residue after driving o:g the liberated phospliorus corresponds approximately, to the forinula $5(CaO).P_2O_5.SiO_2$ - 5. Process of rendering useful insoluble

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Terms	Documents
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